VOL. XXIV. [NOVEMBER, 1902.] NO. 11.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, NO. 70.]

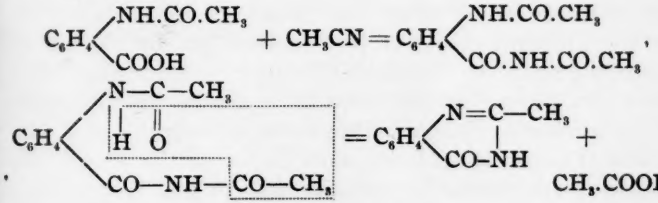
THE SYNTHESIS OF ALKYLKETODIHYDROQUINAZOLINES FROM ANTHRANILIC NITRILE.[1]

BY MARSTON TAYLOR BOGERT AND WILLIAM FLOWERS HAND.

Received July 31, 1902.

THEORETICAL PART.

BOGERT AND GOTTHELF have already shown[2] that ketodihydroquinazolines may be prepared by heating together in sealed tubes anthranilic acid, or its acyl derivatives, with a nitrile, and the reactions there suggested in explanation of this synthesis, taking the case where an acylanthranilic acid was the starting-point, were as follows:



It will be seen upon examining the structure of the hypo-

[1] Read before the New York Section of the American Chemical Society, at its meeting January 24, 1902.

[2] This Journal, **22**, 129 and 522; **23**, 611.

thetical intermediate product, the secondary amide, that the —CO—NH—CO—group being symmetrical should be formed equally well from RCN + R'.COOH as from R'CN + R.COOH; in other words, as the condensation takes place solely between the CN and COOH it is immaterial which radical carries the CN and which the COOH. This same secondary amide should therefore result when acetylanthranilic nitrile is heated with acetic acid, as follows:

$$C_6H_4\begin{cases}NH.CO.CH_3\\CN\end{cases} + CH_3.COOH = C_6H_4\begin{cases}NH.CO.CH_3\\CO.NH.CO.CH_3\end{cases}.$$

At higher temperatures then, acetic acid would split off, as indicated, with production of the quinazoline body, and we have in this manner prepared a number of the quinazolines in question, the products being in every case identical with the compounds obtained from anthranilic acid already described in the articles referred to.

The alkylketodihydroquinazolines may therefore be prepared either from anthranilic acid or from the corresponding nitrile. In cases where the *o*-amino acid is best obtained by saponification of the nitrile, it is convenient to be able to pass directly to the quinazoline from the nitrile without having to prepare the acid at all, thereby saving one step in the synthesis. We have thus prepared quinazolines from homoanthranilic nitrile.

The starting-point for our work was *o*-nitraniline, from which *o*-nitrobenzonitrile was prepared by the Sandmeyer reaction, the yield being excellent. The nitronitrile can be entirely freed from precipitated mineral cyanides by crystallizing from boiling carbon tetrachloride in which the latter are insoluble. This method of purification had been worked out by one of us before the article by Friedländer[1] came to our attention. The latter uses benzene as the means of separating the nitronitrile from the mineral cyanides, but we do not consider this so good a solvent as carbon tetrachloride, since the nitronitrile is much less soluble in cold carbon tetrachloride than in cold benzene, and where the latter is used much more of the compound is left in the mother-liquors. The old process of purification by distillation

[1] *Monatsh. Chem.*, **19**, 627 (1898).

in a current of superheated steam may therefore be abandoned.[1]

The reduction of the nitronitrile is very readily accomplished by the use of stannous chloride and hydrochloric acid, with proper regulation of the temperature; the chloride of the aminonitrile then being precipitated by adding an excess of concentrated hydrochloric acid,[2] the tedious precipitation of the tin by hydrogen sulphide being thus wholly avoided. The free base may be recovered from its chloride by treatment with ice-cold alkali, collecting the base in ether; or, by adding an excess of strong ammonia water to the aqueous solution of the chloride the free base is immediately precipitated, and when washed well with cold water is practically pure. By this process, we have obtained yields of nearly 90 per cent. of that theoretically obtainable from the nitronitrile, and without a sign of saponification, no amide being found in any case, contrary to the experience of Pinnow and Müller,[3] Pinnow and Saemann,[4] and Friedländer.[5]

The anthranilic nitrile thus obtained was heated in sealed tubes with glacial formic acid, and with the anhydrides of acetic, propionic, normal butyric, isobutyric and isovaleric acid. With formic acid no satisfactory results were obtained. In all the other cases the quinazoline was obtained as expected, although the yields are not so good as from anthranilic acid. By using the acid anhydrides, the first products of the reaction are the acylanthranilic nitriles and the fatty acids, which then react at higher temperatures with production of the quinazolines. The presence of any water in the tubes is thus avoided and but little tar is produced.

Some of the acylanthranilic nitriles were isolated in the pure state and further investigated. Like the quinazolines obtainable from them, their melting-points *de*crease with *in*creasing molecular weight, the iso-compounds melting higher than those with normal structure. As it was possible that the formation of the quinazolines was due to a rearrangement of the isomeric acylanthranilic nitriles as follows:

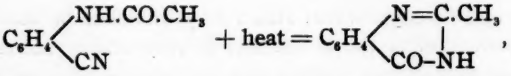
[1] Pinnow and Müller: *Ber. d. chem. Ges.*, **28**, 149 (1895); Pinnow and Saemann: *Ibid.*, **29**, 623 (1896).

[2] As recommended by Friedlander, *loc. cit.*

[3] *Loc. cit.*

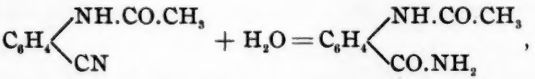
[4] *Loc. cit.*

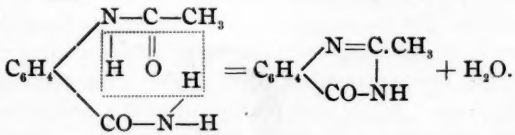
[5] *Loc. cit.*



the acetylanthranilic nitrile, was heated for some time above its melting-point, and it was also heated in sealed tubes in toluene solution; but in neither case was any rearrangement noted. Nevertheless, some of these acylanthranilic nitriles, notably the higher ones, when in aqueous or alcoholic solution, show a decided tendency to pass over into the quinazoline, probably by addition and splitting off of the elements of water somewhat in the manner outlined in the reaction below.

Weddige[1] has already shown that acylanthranilamides can be readily condensed to quinazolines by the action of heat, acids or alkalies. As the acyl groups in these acylanthranilic nitriles are not readily split off, it seemed possible that we might pass direct from these latter substances to the quinazolines without separation of the intermediate amide and without the use of sealed tubes; and by the action of a warm alkaline hydrogen dioxide solution this change was accomplished with ease and rapidity, the yield of quinazoline usually being very large, and the only purification necessary being a single crystallization from water or dilute alcohol. Alkali alone, or hydrogen dioxide alone, we did not find to be nearly so efficient as the combination of the two. The reactions which occur in this synthesis are probably as follows:





The ease with which anthranilic nitrile may be converted into a quinazoline by the action of acetic anhydride suggests the possibility of obtaining a similar condensation by the action of acetic anhydride upon *o*-aminobenzaldoximes, the excess of anhydride changing the oxime to the nitrile when the other reactions out-

[1] *J. prakt. Chem.*, [2] **31**, 124 (1885); **36**, 141 (1887).

lined will take place with production of the quinazoline. We shall test this experimentally and communicate our results in a later article.

In conclusion, our experiments herein recorded indicate that alkylketodihydroquinazolines may be prepared:

(1) By heating anthranilic nitrile in sealed tubes with aliphatic acid anhydrides.

(2) By warming acylanthranilic nitriles with alkaline hydrogen dioxide solution.

EXPERIMENTAL PART.

o-Nitrobenzonitrile.

For the preparation of *o*-nitrobenzonitrile, the following process was found to give the best results:

13.8 grams finely pulverized *o*-nitraniline are treated with 17.5 cc. concentrated hydrochloric acid (sp. gr. 1.187) and the mass stirred until all is changed to the white chloride, taking care to crush up all lumps of *o*-nitraniline in order that the conversion to the chloride may be complete. 500 cc. of water are then added all at once and the mixture stirred thoroughly, causing the dissociation of the chloride and the separation of the free base in fine flocks which diazotize much more rapidly than the finely pulverized nitraniline. The suspended nitraniline is then diazotized by adding a solution of 7 grams sodium nitrite dissolved in 40 cc. water, stirring constantly with a turbine. No external cooling is necessary during the operation as the diazo-body is remarkably stable at ordinary temperatures, no appreciable decomposition occurring even on standing forty-eight hours at laboratory temperature, and cooling only retards the diazotizing and diminishes the yield of nitronitrile. At least one hour should be occupied in adding the sodium nitrite solution, and the mass should then be stirred for another hour, when all the orange nitraniline should be changed to the light-colored flocculent diazo-compound and starch iodide paper should still show the presence of an excess of nitrous acid. If the vessel then be allowed to stand for a few moments, any undiazotized nitraniline will collect on the bottom, and by careful decantation the suspended diazo-body may be poured off from the heavier nitraniline. Although with careful manipulation but little nitraniline escapes diazotizing, yet it is

advisable to decant from it at this point, as otherwise it follows the nitronitrile and must be separated from it later.

The suspended diazo-body is then poured very slowly into a cuprous potassium cyanide solution, prepared from 25 grams crystallized copper sulphate, 150 cc. water and 28 grams 96 per cent. potassium cyanide (carried out under a hood, on account of the cyanogen evolved). The cuprous potassium cyanide should be maintained at about 90° and stirred constantly during the addition of the diazo solution. The yield of nitronitrile depends largely upon this part of the operation. If the diazo solution is added very slowly with vigorous stirring, and the temperature kept at 90°-100°, the yield will be large; rapid addition of the diazo mixture, or allowing the temperature of the cyanide solution to sink much below 90°, diminishes the yield considerably. When all the diazo solution has been added, the mixture is boiled for a few minutes over the open flame and filtered through a hot-water funnel. On cooling, the nitronitrile crystallizes from the filtrate in long yellow needles mixed with considerable cuprous potassium cyanide. A large amount of the nitrile remains behind in what appears to be tar. By extracting this with boiling water so long as crystals separate from the filtrate, on cooling, the rest of the nitrile may be recovered. The crystals obtained by extracting the tar are practically pure and free from mineral cyanides. The actual amount of insoluble tar remaining after these extractions is very small.

The crude crystals are washed well with cold water, dried and pulverized. By extracting this dry material with boiling carbon tetrachloride, the nitronitrile is readily dissolved while the mineral cyanides remain behind absolutely insoluble. From the carbon tetrachloride filtrate, on cooling, the nitronitrile crystallizes out, almost completely, in beautiful golden yellow scales, carrying any unseparated nitraniline, and the amount of the latter substance present may be roughly judged by the depth of color of the crystals and the extent of the orange-colored ring upon the filter-paper above them when they are filtered out. By recrystallization from boiling moderately dilute acetic acid, the nitraniline is removed and the nitronitrile obtained in nearly colorless crystals (m. p. 109°). By further crystallization from dilute acetic acid, or from water, the melting-point may be raised to 109.5° at which

point it remains constant (all melting-points recorded in this article were determined with standardized short-scale Anschütz thermometers, the entire mercury column being immersed in the heating medium).

The authors have repeatedly obtained 12 grams of the crude nitronitrile from 13.8 grams of the nitraniline, a yield of 87 per cent. of the weight of the nitraniline used, and the yield is equally good when working with five to ten times the above charges. The yield of pure nitronitrile (m. p. 109.5°) amounts to about 70 per cent. of the weight of the nitraniline used. As to the amount of mineral cyanide carried down with the nitronitrile—of 285 grams crude nitrile obtained in one experiment, 28 grams consisted of mineral matter insoluble in boiling carbon tetrachloride.

The process outlined above is based upon that of Sandmeyer,[1] with certain improvements suggested by Pinnow and Müller[2] and by Friedländer,[3] together with some modifications of our own. Pinnow and Müller[4] recommend the use of much more concentrated solutions, but their process was far less satisfactory in the hands of the writers than the one given above. So little water is used in their method that the diazo solution forms a stiff paste which it is difficult to stir properly, and the yield of crude nitrile is smaller, besides being richer in mineral cyanides.

Pure *o*-nitrobenzonitrile crystallizes from dilute acetic acid or from water in feathery bunches of fine colorless needles, occasionally united in transparent films with comb-like edges; from carbon tetrachloride it crystallizes in a web of colorless dazzling tinsel-like filaments of iridescent luster, so firmly interwoven that, after pouring out the carbon tetrachloride, it may be removed from the beaker in a single mass which is not easily torn apart. It is very readily soluble in chloroform, acetone, ethyl acetate; easily in methyl alcohol, ethyl alcohol, ethyl nitrate, absolute ether, glacial acetic acid, benzene and nitrobenzene; slowly soluble in cold isoamyl alcohol, dissolving rapidly when heated; difficultly soluble in cold water, moderately soluble on boiling; very slightly soluble in cold carbon tetrachloride, quite readily in hot; difficultly soluble in cold oil of turpentine, easily in hot; difficultly soluble in

[1] *Ber. d. chem. Ges.*, **18**, 1492 (1885).
[2] *Loc. cit.*
[3] *Loc. cit.*
[4] *Loc. cit.*

boiling carbon bisulphide, petroleum ether or benzine. It dissolves very slowly in cold concentrated hydrochloric acid and can be reprecipitated unchanged (m. p. 109.5°) by diluting with water.

o-Aminobenzonitrile (*Anthranilic Nitrile*).

According to our experience, the reduction of the nitronitrile can be accomplished more satisfactorily with stannous chloride and hydrochloric acid than with tin and hydrochloric acid.

The following process, based upon the method of Pinnow and Saemann[1] and embodying certain suggestions due to Friedländer[2], has given excellent results.

500 grams stannous chloride are dissolved in 425 cc. concentrated hydrochloric acid diluted with 7.5 cc. of water, and the solution is stirred vigorously with a turbine while 100 grams of the nitronitrile are gradually added at such a rate that the temperature of the solution remains at 20°-30°, occasional cooling with ice being necessary. Below 20° the reduction proceeds very slowly. As the action progresses the nitronitrile gradually dissolves, and the reduction should be complete in a few hours. If the chloride of the aminonitrile begins to separate before the completion of the reduction it can be brought into solution again by careful addition of water. When all the nitronitrile has been reduced a large volume of concentrated hydrochloric acid is added and the mixture is left for twelve to eighteen hours at 0°. Nearly all of the aminonitrile will thus be precipitated as the chloride, in fine white granular crystals which can be filtered out through asbestos. The amount of this chloride remaining in the acid mother-liquor is usually very small and not sufficient to pay for the time and trouble necessary to recover it. Of course, if the reducing solution be too greatly diluted with water, the precipitation with hydrochloric acid will be much less complete, and it may then be advisable to work over the mother-liquor. In one of our experiments there was precipitated by the hydrochloric acid an amount of aminonitrile chloride equivalent to a yield of 80 per cent. of that theoretically obtainable from the nitronitrile, while from the acid mother-

[1] *Loc. cit.*
[2] *Loc. cit.*

liquor there was recovered but 5 per cent. more, making the total yield 85 per cent. of the theoretical. The precipitated chloride is washed free from tin with concentrated hydrochloric acid, sucked as dry as possible, and the free base liberated by either of the following methods:

(1) The chloride is added to a mixture of ice and ether contained in a separatory funnel. Sodium hydroxide solution is poured in to alkaline reaction, the mixture well shaken and the ether poured off, the residual aqueous solution being extracted three or four times more with ether. The ethereal extracts are combined, dried with calcium chloride, the ether distilled off, and the brown liquid residue placed *in vacuo* over concentrated sulphuric acid where it soon solidifies in a light brown crystalline cake melting at 49° C.

(2) The chloride may be added direct to an excess of moderately dilute ammonia water, the precipitated base washed with water till free from ammonium chloride, dried and crystallized from carbon bisulphide. The yield of pure aminonitrile by this process is usually at least 85 per cent. of the theoretical. We have not observed in any case the formation of nitro- or amino-amide, the crystals which separated during reduction being invariably only the chloride of the amino-nitrile, the free base obtained from them being always instantly and completely soluble in cold benzene (in which the *o*-nitro- and *o*-aminobenzamides are difficultly soluble).

The melting-point of the crude aminonitrile is 49°; on recrystallization this may be raised to 49.5° at which point it remains constant. Friedländer[1] gives the melting-point as 50°-51°.

Pure anthranilic nitrile crystallizes in colorless glassy monoclinic prisms. By slow cooling of a carbon bisulphide solution, we have obtained some superb prisms of light yellow cast, two inches long by a quarter of an inch thick and perfectly formed. It is very easily soluble in chloroform, methyl alcohol, ethyl alcohol, ethyl nitrate, absolute ether, acetone, ethyl acetate, carbon bisulphide, benzene, nitrobenzene and pyridine; easily soluble in carbon tetrachloride and amyl alcohol; moderately soluble in cold oil of turpentine, very easily on boiling; difficultly soluble in cold water, moderately soluble at boiling-point; insoluble in cold con-

[1] *Loc. cit.*

centrated ammonia water, moderately soluble boiling; insoluble in cold petroleum ether or benzine, slightly soluble boiling. From boiling water the substance often separates as an oil which only slowly solidifies on standing. Occasionally, glassy blades may be obtained from water, but if these are left in the solution for a few days they become white and opaque and then show a lower melting-point (46°-47°). The carbon bisulphide solution is very sensitive to changes of temperature; from a solution prepared at the ordinary temperature the nitrile may be crystallized out almost completely by cooling slowly in a freezing-mixture; and large crystals which have separated by slow evaporation of the solvent at the ordinary temperature may all be redissolved quite rapidly by a slight rise in the temperature of the laboratory.

Hydrochloride of Anthranilic Nitrile.

To prepare this chloride, the nitrile was dissolved in dry ether and a stream of dry hydrochloric acid gas passed in. The chloride precipitated immediately, and was filtered out, washed with dry ether, and recrystallized from glacial acetic acid. These crystals decompose when heated slowly, but can be melted if heated quickly. They are instantly dissociated by water and give off hydrochloric acid even in the air. They dissolve quite easily in absolute alcohol, are sparingly soluble in boiling toluene, moderately soluble in glacial acetic acid (with partial dissociation), and are apparently insoluble in chloroform, carbon tetrachloride, benzene, absolute ether, ligroin or acetone.

Pinnow and Müller[1] state that this chloride crystallizes in beautiful tablets which are quite stable, although they also admit that they tend to dissociate in aqueous solution, while Pinnow and Saemann[2] attempted to separate anthranilic nitrile from the corresponding amide by crystallizing their chlorides from water. Our experience concerning the stability in aqueous solution of the chloride of anthranilic nitrile is quite at variance with these statements. In concentrated hydrochloric acid the chloride appears to be quite stable, however.

[1] *Loc. cit.*
[2] *Loc. cit.*

The Preparation of 2-Alkyl-4-ketodihydroquinazolines by Heating Anthranilic Nitrile in Sealed Tubes with Aliphatic Acids or Their Anhydrides.

(1) *Anthranilic Nitrile and Glacial Formic Acid.*—These two substances were heated together in sealed tubes for eight hours at 270°-284°, but no quinazoline could be found in the reaction product.

(2) *Anthranilic Nitrile and Acetic Anhydride.* Tube 1.—Four grams of the nitrile and 3 cc. of acetic anhydride were heated in a sealed tube for six hours at 175°, and then for five hours at 200°. There was no pressure in the tube when cold, and the contents consisted of a yellow crystalline mass of fine felted needles. This crystalline mass was repeatedly washed with ether, the residue crystallized from nitrobenzene, the crystals obtained, washed with naphtha, then with petroleum ether, dried, and recrystallized from boiling water, containing some bone-black. From the filtrate, on cooling, there separated short glassy needles of the 2-methyl-4-ketodihydroquinazoline, melting sharply at 239° and identical in all respects with that obtained by the action of acetic anhydride and acetonitrile upon anthranilic acid. A mixture of the products obtained from these two sources showed the same sharp melting-point as when the two were melted separately.

The crystals are very easily soluble in glacial acetic acid or in concentrated potassium hydroxide solution; they are difficultly soluble in petroleum ether, naphtha, carbon tetrachloride, ethyl nitrate, ether, acetic anhydride, carbon bisulphide, benzene, xylene, cymene, or concentrated hydrochloric acid; difficultly soluble in cold water, chloroform, acetone, ethyl acetate, or oil of turpentine, moderately soluble in the same solvents at the boiling-point; difficultly soluble in cold methyl, ethyl or isoamyl alcohols, glycerol, or nitrobenzene, easily soluble in the same on boiling. An alcoholic solution of the base, treated with concentrated hydrochloric acid, gives an immediate crystalline precipitate of the chloride. The latter sublimes unchanged, without melting, and is less soluble in dilute hydrochloric acid than in water. The crystals of the free base and also of the chloride frequently show a faint yellowish green cast.

Tube 2.—2.5 grams of the nitrile and 3 cc. of the anhydride were heated for ten hours at 274°-282°, the crude product dissolved in hot alcohol, the solution bone-blacked, filtered hot, and the filtrate concentrated. On cooling, crystals of the quinazoline compound separated, melting at 237.5° to 238.5°. Some of the purified crystals (m. p. 239°) were dried to constant weight at 135° and analyzed:

I. 0.1814 gram substance gave 29.1 cc. nitrogen at 23° and 748 mm. = 17.78 per cent. nitrogen.

II. 0.2000 gram substance gave 0.4960 gram carbon dioxide and 0.0900 gram water = 67.63 per cent. carbon and 5 per cent. hydrogen.

	Calculated for $C_9H_8ON_2$.	Found. I.	II.
Nitrogen	17.50	17.78	....
Carbon	67.50	....	67.63
Hydrogen	5.00	....	5.00

The *picrate*, recrystallized from water, forms yellow prisms (m. p. 207.5°-208.5°).

(3) *Anthranilic Nitrile and Propionic Anhydride.* Tube 1.—2.5 grams of the nitrile and 3 cc. of the anhydride were heated for five hours at 250°, and then for three hours at 275°-280°. On opening the tube no pressure was evident, and the contents were dissolved in boiling alcohol, the solution bone-blacked, filtered hot, and the filtrate concentrated. On cooling, crystals separated melting at 220°-231°, brownish in color and evidently a mixture. Washed with boiling water and recrystallized from dilute alcohol, brownish crystals were obtained melting at 220°-232°. As the amount of these crystals was small, further purification was deemed useless, the reaction being evidently incomplete.

Tube 2.—This tube contained the same charge as Tube 1, but was heated for six and a half hours at 270°-280°, then two hours at 230°, and finally for six hours longer at 274°-285°. There was no pressure in the tube when cold, and the contents were repeatedly crystallized from carbon tetrachloride, yielding crystals which were easily soluble in boiling carbon tetrachloride but difficultly soluble in it cold, and which melted at 232.5°-233.5°, softening somewhat at 231°. These crystals are identical in all their properties with the 2-ethyl-4-ketodihydroquinazoline prepared from anthranilic acid, the melting-point of which is 234°.

The *picrate* melted at 193°-194°, while that obtained from anthranilic acid melted a trifle lower (191°-192°).

(4) *Anthranilic Nitrile and Normal Butyric Anhydride.* Tube 1.—The nitrile and anhydride were heated together for three hours at 160°-198°, and then for five hours at 192°-220°. The contents of the tube appeared gray and crystalline, and by extracting with boiling water, crystals were obtained melting at 198°, which, when recrystallized from water, formed fine colorless needles, identical in all their properties with the 2-*n*-propyl-4-ketodihydroquinazoline prepared from anthranilic acid.

Tube 2 contained 2.5 grams of the nitrile and 3 cc. of *n*-butyric anhydride, and was heated four hours at 130°-211°, then for seven hours at 210°-212°, and finally for three hours longer at 215°-255°. The product was dissolved in boiling alcohol, the solution bone-blacked, filtered hot, and the filtrate concentrated; on cooling, small crystals of the quinazoline separated, which, when recrystallized from dilute alcohol, melted sharply at 200°-200.8°.

The *picrate*, after repeated crystallization, showed a melting-point of 184.5°-185°. Gotthelf[1] gives the melting-point as 183°-184°.

(5) *Anthranilic Nitrile and Isobutyric Anhydride.*—2.5 grams of the nitrile and 3 cc. of the anhydride were heated for six hours at 224°-229° and then for six and a half hours at 275°. On cooling, no pressure was evident in the tube. The crude product was worked up in exactly the same manner as described for Tube 2 above, the crystals which separated from the alcoholic solution being recrystallized from dilute alcohol. Colorless needles were thus obtained, melting at 231.5°-232°, agreeing in all their properties with the 2-isopropyl-4-ketodihydroquinazoline obtained from anthranilic acid.

The *picrate* melts at 208.5°-209.5°. The melting-point of 213°-214° recorded for this picrate by Gotthelf[2] is evidently a mistake, as we have tested his own product and found its melting-point to be 208°-208.5°.

(6) *Anthranilic Nitrile and Isovaleric Anhydride.*—2.5 grams of the nitrile and 3 cc. of the anhydride were heated for six hours

[1] This Journal, **23**, 611.
[2] *Loc. cit.*

Tube 2.—2.5 grams of the nitrile and 3 cc. of the anhydride were heated for ten hours at 274°-282°, the crude product dissolved in hot alcohol, the solution bone-blacked, filtered hot, and the filtrate concentrated. On cooling, crystals of the quinazoline compound separated, melting at 237.5° to 238.5°. Some of the purified crystals (m. p. 239°) were dried to constant weight at 135° and analyzed:

I. 0.1814 gram substance gave 29.1 cc. nitrogen at 23° and 748 mm. = 17.78 per cent. nitrogen.

II. 0.2000 gram substance gave 0.4960 gram carbon dioxide and 0.0900 gram water = 67.63 per cent. carbon and 5 per cent. hydrogen.

	Calculated for $C_9H_8ON_2$.	Found. I.	Found. II.
Nitrogen	17.50	17.78	....
Carbon	67.50	....	67.63
Hydrogen	5.00	....	5.00

The *picrate,* recrystallized from water, forms yellow prisms (m. p. 207.5°-208.5°).

(3) *Anthranilic Nitrile and Propionic Anhydride.* Tube 1.—2.5 grams of the nitrile and 3 cc. of the anhydride were heated for five hours at 250°, and then for three hours at 275°-280°. On opening the tube no pressure was evident, and the contents were dissolved in boiling alcohol, the solution bone-blacked, filtered hot, and the filtrate concentrated. On cooling, crystals separated melting at 220°-231°, brownish in color and evidently a mixture. Washed with boiling water and recrystallized from dilute alcohol, brownish crystals were obtained melting at 220°-232°. As the amount of these crystals was small, further purification was deemed useless, the reaction being evidently incomplete.

Tube 2.—This tube contained the same charge as Tube 1, but was heated for six and a half hours at 270°-280°, then two hours at 230°, and finally for six hours longer at 274°-285°. There was no pressure in the tube when cold, and the contents were repeatedly crystallized from carbon tetrachloride, yielding crystals which were easily soluble in boiling carbon tetrachloride but difficultly soluble in it cold, and which melted at 232.5°-233.5°, softening somewhat at 231°. These crystals are identical in all their properties with the 2-ethyl-4-ketodihydroquinazoline prepared from anthranilic acid, the melting-point of which is 234°.

The *picrate* melted at 193°-194°, while that obtained from anthranilic acid melted a trifle lower (191°-192°).

(4) *Anthranilic Nitrile and Normal Butyric Anhydride.* Tube 1.—The nitrile and anhydride were heated together for three hours at 160°-198°, and then for five hours at 192°-220°. The contents of the tube appeared gray and crystalline, and by extracting with boiling water, crystals were obtained melting at 198°, which, when recrystallized from water, formed fine colorless needles, identical in all their properties with the 2-*n*-propyl-4-ketodihydroquinazoline prepared from anthranilic acid.

Tube 2 contained 2.5 grams of the nitrile and 3 cc. of *n*-butyric anhydride, and was heated four hours at 130°-211°, then for seven hours at 210°-212°, and finally for three hours longer at 215°-255°. The product was dissolved in boiling alcohol, the solution bone-blacked, filtered hot, and the filtrate concentrated; on cooling, small crystals of the quinazoline separated, which, when recrystallized from dilute alcohol, melted sharply at 200°-200.8°.

The *picrate*, after repeated crystallization, showed a melting-point of 184.5°-185°. Gotthelf[1] gives the melting-point as 183°-184°.

(5) *Anthranilic Nitrile and Isobutyric Anhydride.*—2.5 grams of the nitrile and 3 cc. of the anhydride were heated for six hours at 224°-229° and then for six and a half hours at 275°. On cooling, no pressure was evident in the tube. The crude product was worked up in exactly the same manner as described for Tube 2 above, the crystals which separated from the alcoholic solution being recrystallized from dilute alcohol. Colorless needles were thus obtained, melting at 231.5°-232°, agreeing in all their properties with the 2-isopropyl-4-ketodihydroquinazoline obtained from anthranilic acid.

The *picrate* melts at 208.5°-209.5°. The melting-point of 213°-214° recorded for this picrate by Gotthelf[2] is evidently a mistake, as we have tested his own product and found its melting-point to be 208°-208.5°.

(6) *Anthranilic Nitrile and Isovaleric Anhydride.*—2.5 grams of the nitrile and 3 cc. of the anhydride were heated for six hours

[1] This Journal, **23**, 611.
[2] *Loc. cit.*

at 224°-229° and then for six and a half hours at 275°, there being no pressure in the tube when cold. The crude product was treated in the manner just described, the first crystals obtained being recrystallized from dilute alcohol, when they showed a melting-point of 194°-195°, and proved to be identical with 2-isobutyl-4-ketodihydroquinazoline prepared from anthranilic acid.

The *picrate* melted at 188.5°-189.5°. The melting-point recorded by Gotthelf[1] for the same substance is 192. It is not easy to determine the melting-points of these picrates accurately, as they generally darken and soften several degrees below the actual melting-point.

The Preparation of Acyl Derivatives of Anthranilic Nitrile.

(1) *The Action of Glacial Formic Acid upon Anthranilic Nitrile.*—Five cc. of absolute formic acid were poured over five grams of the nitrile, causing the latter to dissolve with absorption of considerable heat. The solution was gently boiled on the sand-bath for two hours and then allowed to cool. The product was a yellow crystalline cake, a portion of which when heated to 200° appeared to suffer decomposition with evolution of gas. The cake itself is composed of a mixture of various substances and we have separated from it white, warty masses easily soluble in boiling water; also long yellow needles, apparently insoluble in boiling water and difficultly soluble in boiling alcohol, together with a flocculent yellow substance soluble in 95 per cent. alcohol. None of these products could be secured in sufficient amount or purity to render an analysis of any value. The white, warty masses are evidently the formyl derivative of the nitrile, since a quinazoline can be obtained from them on treatment with warm, alkaline hydrogen dioxide solution.

(2) *The Action of Acetic Anhydride upon Anthranilic Nitrile.*—Anthranilic nitrile dissolves quite rapidly in acetic anhydride with the absorption of considerable heat; this heat is soon given off again and the solution gradually warms up to the boiling-point of the anhydride; on cooling down again a solid crystalline cake is formed. This cake is melted and gently boiled for a few hours

[1] *Loc. cit.*

on the sand-bath, the hot liquid is poured into boiling water, the mixture boiled for a few minutes and the solution filtered hot. From the filtrate, on cooling, the acetyl derivative crystallizes in long, white, silky needles (m. p. 132.5), as given by Pinnow and Saemann.[1] By heating for some time above its melting-point, no rearrangement of the compound to the isomeric quinazoline was noted. The crystals are very easily soluble in chloroform, methyl alcohol, ethyl alcohol, isoamyl alcohol, ethyl nitrate, ether, acetone, ethyl acetate, glacial acetic acid, acetic anhydride, or nitrobenzene; easily in carbon bisulphide, benzene, or oil of turpentine; moderately in carbon tetrachloride or in cold water, easily soluble in the latter at the boiling-point; insoluble in cold petroleum ether or benzine, difficultly soluble in the same at the boiling-point. Long boiling of the aqueous solution tends to prevent the crystallization of the substance, giving a milky solution which slowly deposits a fine floury sediment. It is not readily extracted from its aqueous solution by ether. From petroleum solvents, it crystallizes in pulpy masses of minute needles difficult to filter and which pack down upon the filter-paper into a sort of skin. Good crystals may be obtained from water, and also from mixtures of naphtha and chloroform, naphtha and ether, or chloroform and carbon tetrachloride. It can be slowly sublimed at 100° in colorless transparent needles, and is volatile with steam. Warmed with alkaline hydrogen dioxide solution, or heated in a sealed tube with glacial acetic acid or acetic anhydride, 2-methyl-4-ketodihydroquinazoline is produced. 2.5 grams of the acetyl derivative and 3 cc. of toluene were heated for ten hours at 274°-282° without any rearrangement of the acetyl derivative occurring. Toluene was selected as the solvent on account of its inertness and because its boiling-point is near that of acetic anhydride and acetic acid, and also because the quinazolines are difficultly soluble in it.

Once or twice, in the preparation of this acetylanthranilic nitrile, on recrystallizing the crude product from water, there was obtained a small amount of a substance crystallizing in perfect little cubes, of faint yellowish cast, which melted sharply at 91°, but the amount obtained was insufficient for further investigation.

(3) *The Action of Propionic Anhydride upon Anthranilic Nitrile.*—Five grams of the nitrile were mixed with 7 cc. of the

[1] *Loc. cit.*

anhydride. The nitrile dissolved slowly in the anhydride with absorption of considerable heat; the solution then gradually warmed up and on cooling down again solidified in a white crystalline cake. This mass was boiled gently for several hours and the product crystallized from dilute alcohol after bone-blacking. Beautiful, colorless, glassy prisms were thus obtained, melting at 119°. If heated quickly, these crystals melt much lower than this. They liquefy in boiling water. At 100°, they slowly sublime in long colorless needles. They are difficultly soluble in boiling water, nearly insoluble in cold; readily soluble in alcohol. They dissolve in cold 5 per cent. aqueous potassium hydroxide solution, and do not reprecipitate when this solution is made acid with hydrochloric acid; if an excess of strong ammonia water be then added, colorless needles of the original substance are obtained. The compound is volatile with steam. A portion was dried to constant weight *in vacuo* over concentrated sulphuric acid. This gave 16.89 and 16.44 per cent. nitrogen. Calculated for

$$C_6H_4\begin{cases}NHCOC_2H_5\\CN\end{cases}$$, 16.64 per cent.

Heated in a sealed tube with propionic anhydride, or warmed with alkaline hydrogen dioxide solution, 2-ethyl-4-ketodihydroquinazoline is produced.

(4) *The Action of n-Butyric Anhydride upon Anthranilic Nitrile.*—This reaction was carried out in a similar manner to the last, using 5 grams of the nitrile and 8 cc. of the anhydride. The nitrile dissolves slowly with absorption of heat, but does not warm up or appear to change on standing. The solution is boiled for an hour, the crude product crystallized from dilute alcohol and bone-blacked, giving colorless glassy needles or long flattened prisms. By repeated crystallization, a sharp melting-point of 89°-89.5° was recorded. These crystals are difficultly soluble in water, but easily soluble in alcohol, and volatilize with steam. With 5 per cent. aqueous potassium hydroxide solution, followed by hydrochloric acid and ammonia, this compound behaves like the propionyl derivative.

Heated in a sealed tube with *n*-butyric anhydride, or warmed with alkaline hydrogen dioxide solution, 2-*n*-propyl-4-ketodihy-

droquinazoline results. The substance is therefore the *n*-butyryl anthranilic nitrile. Long boiling in aqueous or alcoholic solution tends to change this butyryl derivative to the quinazoline.

(5) *The Action of Isobutyric Anhydride upon Anthranilic Nitrile.*—This reaction was carried out in a manner entirely similar to the last, the crude product being recrystallized from dilute alcohol till the melting-point remained constant at 111°-111.5°. The compound forms long, white, silky needles, which are slowly soluble in cold carbon tetrachloride or benzene, but easily soluble in the same on boiling; difficultly soluble in carbon bisulphide, petroleum ether, or gasoline; easily soluble in cold ether or alcohol. At 100° it slowly sublimes in colorless glistening scales. It is volatile with steam. A sample, dried to constant weight, gave the following results upon analysis: Carbon, 70.21, 70.22; hydrogen, 5.84, 5.83. Calculated for

$C_6H_4\begin{cases}NH.CO.CH(CH_3)_2\\CN\end{cases}$, carbon, 70.21; hydrogen, 6.38.

Heated in a sealed tube with isobutyric anhydride, or warmed with alkaline hydrogen dioxide solution, the product is 2-isopropyl-4-ketodihydroquinazoline.

(6) *The Action of Isovaleric Anhydride upon Anthranilic Nitrile.*—The reaction proceeds in the same manner as noted for the foregoing, but much greater difficulty was experienced in the purification of the crude product, repeated crystallization from dilute alcohol failing to give any substance with constant sharp melting-point. By recrystallizing from carbon tetrachloride, however, beautiful fine needles were produced, melting quite sharply at 105.5°-106.5°, and which are evidently the isovaleryl anthranilic nitrile. They are difficultly soluble in water, readily so in alcohol. In boiling water, they liquefy, and are volatile with steam. Heated in a sealed tube with *i*-valeric anhydride, or warmed with alkaline hydrogen dioxide solution, 2-isobutyl-4-ketodihydroquinazoline is the product.

A portion of the substance, dried to constant weight, gave 14.01 per cent. nitrogen. Calculated for

$C_6H_4\begin{cases}NH.CO.CH.CH_2(CH_3)_2\\CN\end{cases}$, 13.86 per cent.

The Preparation of 2-Alkyl-4-Ketodihydroquinazolines by the Action of Warm Alkaline Hydrogen Dioxide Solution upon Acylanthranilic Nitriles.

The compounds obtained in this manner were, in every case, identical with the corresponding substances prepared from either anthranilic acid, its nitrile, or their acyl derivatives, in sealed tubes, as already described.

(1) *4-Ketodihydroquinazoline.*—Some of the crude formylanthranilic nitrile already mentioned was dissolved in 10 per cent. potassium hydroxide solution, some hydrogen dioxide solution (3 per cent.) added, and the mixture warmed at 40°-50° for an hour and a half. The solution was then filtered from a small amount of insoluble matter, the filtrate neutralized with hydrochloric acid, excess of strong ammonia water added, the solution evaporated to dryness, the residue dissolved in 99 per cent. alcohol and the solution concentrated. On cooling, crystals separated, which were filtered out, washed, dried and sublimed, giving beautiful white crystals (m. p. 215.5°-216.5°). Knape[1] gives the melting-point of 4-ketodihydroquinazoline as 211°-212°. Not sufficient of the substance was available for an analysis.

The *picrate* forms long yellow needles or plates, melting at 203.5°-204.5°, softening somewhat at 202°.

(2) *2-Methyl-4-Ketodihydroquinazoline.*—5.6 grams acetylanthranilic nitrile were mixed with 75 cc. hydrogen dioxide solution and 20 cc. of a 10 per cent. potassium hydroxide solution, and the mixture warmed at 30°-45°. In about fifteen minutes complete solution resulted, and fine white needles then began to separate, the separation being apparently complete after warming about fifteen minutes longer, since further addition of hydrogen dioxide or of potassium hydroxide caused no increase in the precipitate. These needles dissolve instantly upon the addition of a small amount of strong potassium hydroxide solution, and may be reprecipitated by carefully neutralizing with hydrochloric acid, but any excess of acid redissolves the precipitate again. From this acid solution it may be completely thrown down by adding an excess of strong ammonia water. The voluminous white pre-

[1] *J. prakt. Chem.*, (2) **43**, 209 (1891).

cipitate thus obtained is crystallized from boiling water and bone-blacked, yielding beautiful glassy prisms of the 2-methyl-4-ketodihydroquinazoline (m. p. 239°). From 5.6 grams of the acetylanthranilic nitrile there was obtained 3.47 grams of the pure quinazoline compound. Some of the substance was dried to constant weight at 100°-140° and analyzed, with the following results: Carbon, 67.36, 67.32; hydrogen, 5.08, 5.02; nitrogen, 17.28, 17.47. Calculated: Carbon, 67.50; hydrogen, 5.00; nitrogen, 17.50.

When the acetylanthranilic nitrile is heated with hydrogen dioxide alone, or with alkali alone, the yield of quinazoline is not nearly so good.

The *picrate* from the above crystals separated in clusters of reddish prisms (m. p. 206°).

(3) *2-Ethyl-4-Ketodihydroquinazoline.*—1.1 grams propionylanthranilic nitrile were warmed with alkaline hydrogen dioxide solution as just indicated, the temperature being kept at 30°-65°. A clear solution was not obtained, but the propionyl derivative gradually changed to a bulky white mass of pearly scales instantly soluble in a little strong caustic alkali. The alkaline solution was treated with an excess of hydrochloric acid, then with an excess of concentrated ammonia water. The precipitate thus produced was recrystallized from water, giving fine white hairy needles of the 2-ethyl-4-ketodihydroquinazoline. The melting-point of these needles was rather low, probably because the propionylanthranilic nitrile used in the reaction was itself not perfectly pure (second-crop crystals). Recrystallization failed to raise the melting-point above 232°, while the same compound prepared from anthranilic acid melted at 234°. The yield of first-crop crystals was 0.836 gram.

The *picrate* crystallized in yellow scales (m. p. 191°-192°).

(4) *2-n-Propyl-4-Ketodihydroquinazoline.*—It was prepared from *n*-butyrylanthranilic nitrile and alkaline hydrogen dioxide solution at 30°-80°, in a similar manner to the last. The crude product was recrystallized from dilute alcohol, giving a woolly mass of fine colorless needles (m. p. 201°-202°), of 2-*n*-propyl-4-ketodihydroquinazoline.

The *picrate* crystallized in bunches of long yellow needles

(m. p. 184°-184.5°); difficultly soluble in cold water, moderately in boiling; quite soluble in cold alcohol, easily in boiling.

(5) *2-Isopropyl-4-Ketodihydroquinazoline.*—About 2 grams of the isobutyrylanthranilic nitrile, 25 cc. hydrogen dioxide solution, and 25 cc. 10 per cent. potassium hydroxide solution, were warmed together at 50°, all gradually dissolving. The solution was precipitated by hydrochloric acid, the precipitate not readily dissolving in an excess of the precipitant, and excess of strong ammonia water was then added. The bulky white precipitate which was thrown down, when recrystallized from dilute alcohol, appeared as long, colorless, silky hairs (m. p. 233°), readily identified as the 2-isopropyl-4-ketodihydroquinazoline.

The *picrate* crystallized from alcohol in yellow prisms (m. p. 208°-208.5°), at which point they turned brown and appeared to decompose. They began to darken at 205°.

(6) *2-Isobutyl-4-Ketodihydroquinazoline.*—This substance was prepared from the isovalerylanthranilic nitrile in the manner just outlined. The bulky white precipitate thrown down by ammonia water was recrystallized from dilute alcohol, giving crystals of the quinazoline, melting at 194.5°-195.5°.

The melting-point of the *picrate* was found to be 188°-189°.

In general, the yield of quinazoline obtained by the use of warm, alkaline hydrogen dioxide solution was much better than that resulting from heating the acylanthranilic nitriles in sealed tubes with anhydrides.

ORGANIC LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY, June, 1902.

THE ACTION OF ISO-VALERIC ALDEHYDE UPON ANTIPYRINE.[1]

BY DAVID C. ECCLES.

Received July 14, 1902.

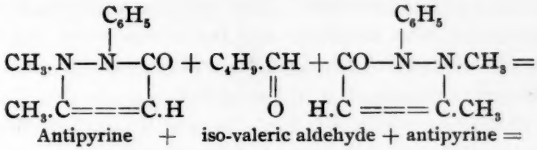
THE investigations of Knorr[2] and Schuftan[3] show that antipyrine is capable of forming condensation products with both aliphatic and aromatic aldehydes. Knorr, by treating a slightly

[1] The work here reported was done in Havemeyer Hall, Columbia University, under the direction of Prof. M. T. Bogert.

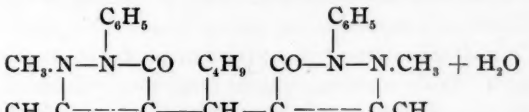
[2] *Ann. Chem.* (Liebig), **238**, 214.

[3] *Ber. d. chem. Ges.*, **1**, 1181, 1189 (1895).

acid, concentrated aqueous solution of antipyrine with benzaldehyde and neutralizing, procured benzylidene-di-antipyrine. Schuftan, at a later date, by using formaldehyde instead of benzaldehyde, produced the corresponding methylene-di-antipyrine. As these condensations take place readily and give good yields of product it was concluded that 1 molecule of iso-valeric aldehyde might also combine with 2 molecules of antipyrine to give valeryl-di-antipyrine, according to this reaction:



Antipyrine + iso-valeric aldehyde + antipyrine =



Valeryl-di-antipyrine + water.

On trial this was found to be the case. The aldehyde and base, mixed in the proportion of 1 molecule of iso-valeric aldehyde and 2 molecules of antipyrine, along with enough hydrochloric acid to give a faintly acid reaction, were heated in a flask connected with a return condenser, for six hours, at 100° C., and then allowed to cool. The resulting oily liquid was poured into a small amount of concentrated potassium hydroxide solution, at once diluted with water and then stirred vigorously. After several hours' standing, an oily layer which separated changed into a white solid. This being filtered off was washed with cold water and then thoroughly dried. On crystallizing it from ligroin its melting-point was found to be 160°-161° C. The yield was about 40 per cent. of the amount calculated from the reaction cited.

The condensation here described was repeated several times and on each occasion the resulting product was composed of fine, white crystals, insoluble in cold water, slightly soluble in hot water and very soluble in alcohol. It was freely soluble in all dilutions of alcohol with water up to two of the latter to one of

the former. Hot naphtha and ligroin readily dissolved it. With hydrochloric acid this new derivative combined to form a hydrochloride and with sulphuric acid to form a sulphate. The hydrochloride was prepared by covering the condensation product with water and adding concentrated hydrochloric acid by drops. The solid slowly went into solution but, after a few minutes' standing, separated again as long, feathery needles. These were quite soluble in water and still more readily in the presence of a slight amount of hydrochloric acid. The sulphate was prepared in a similar manner from sulphuric acid but it was much less soluble and therefore separated more readily and completely.

With ferric chloride the hydrochloride gave a thick, reddish brown precipitate which dried to a brownish powder. This was soluble in alcohol and possessed a sharp astringent taste quite unlike the almost tasteless free valeryl base. This ferric derivative is analogous to ferripyrine—the ferric chloride compound of antipyrine. With Mayer's reagent both the hydrochloride and sulphate gave a white, curdy precipitate. When valeryl-di-antipyrine is warmed with concentrated sulphuric acid and sugar it gives a distinct odor like that of valerianic acid.

A determination of the nitrogen contained in valeryl-di-antipyrine gave 13 per cent. nitrogen. Calculated for $C_{27}H_{32}O_2N_4$, the nitrogen would be 12.3.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NEBRASKA WESLEYAN UNIVERSITY.]

ON THE REDUCTION OF SOME AROMATIC NITRO-COMPOUNDS.

BY F. J. ALWAY AND M. D. WELSH.

Received July 21, 1902.

IN THE following paper we give the results thus far obtained from a study of the reduction of *p*-nitrobenzaldehyde and *m*-nitrobenzaldehyde in neutral solution. As this work is for a few months necessarily interrupted and as we will be unable to continue it together we consider it best to publish the results already at hand. The investigation was undertaken in the hope that we might be able to isolate from the reduction products of the nitro-

benzaldehydes the corresponding N-formylphenyl ethers of the nitrobenzaldoximes,[1] of the formula,

$$NO_2.C_6H_4.CH\overset{O}{\diagdown\!\diagup}N.C_6H_4.CHO.$$

As these ethers, when oxidized, give almost the theoretical yield of the corresponding nitrosobenzaldeyhdes,[2] according to the equation,

$$NO_2.C_6H_4.CH\overset{O}{\diagdown\!\diagup}N.C_6H_4.CHO + O = NO_2.C_6H_4.CHO + ON.C_6H_4.CHO,$$

an economical method of preparing them would make the corresponding nitrosoaldehydes readily accessible compounds. The yield of these ethers obtained by the electrolytic reduction of the nitrobenzaldehydes, dissolved in concentrated sulphuric acid, is unsatisfactory, varying from 20 to 40 per cent. We failed to obtain these ethers by reduction in neutral solution. Various hydroxylaminobenzaldehyde derivatives were formed, all of which on oxidation yielded the corresponding nitroso-compounds.

In a previous article[3] one of us has described some of the phenomena observed when a solution of *p*-nitrobenzaldehyde in boiling water is treated with zinc dust.

By the action of zinc dust upon aromatic nitro-compounds in neutral aqueous or alcoholic solution, with or without addition of ammonium salts, Bamberger[4] has obtained a large number of hydroxylamino-compounds analogous to *β*-phenyl hydroxylamine, $C_6H_5NH.OH$. These are characterized by the ease with which they decompose, yielding a great variety of compounds. Wislicenus[5] has obtained the same compounds by the action of amalgamated aluminum upon the nitro-compounds in ethereal or alcoholic solution. Zinc amalgam with aluminum sulphate solution acts similarly.[6] By the oxidation of the hydroxylamine derivatives the corresponding nitroso-compounds were obtained. The latter are readily volatile with steam and, with the exception of the blue-green 3,4-dimethyl-nitrosobenzene[7] and the yellow

[1] *Ber. d. chem. Ges.*, **20**, 3037 (1896).
[2] *Am. Chem. J.*, **28**, 38.
[3] *Loc. cit.*
[4] *Ber. d. chem. Ges.*, **27**, 1548 (1894).
[5] *Ibid.*, **29**, 494 (1896).
[6] *Ibid.*, **29**, 863 (1896).
[7] *Ann. Chem.* (Liebig), **316**, 2857 (1901).

p-nitrosobenzaldehyde,[1] are colorless in the solid state. When fused or in solution they are green. Bamberger[2] has recently shown that 1-nitroso-2,6-xylene and nitrosomesitylene, whose cold solutions are much less intensely colored than the hot solutions, consist largely of double molecules in the former and of single molecules in the latter. Evidently the green color of the nitroso-compounds depends upon the presence of single molecules.[3] We find that *p*-nitrosobenzaldehyde, unlike the isomeric meta-compound, resembles nitrosomesitylene. Further, it is volatile with steam only when in the monomolecular condition.

The readiness with which aromatic hydroxylamines condense with aldehydes, according to the equation,

$$R.CHO + H{-}\overset{HO}{\overset{|}{N}}.R = R.\overset{O}{\overset{/\backslash}{CH}}{-}N.R + H_2O,$$

has rendered the isolation of the hydroxylaminobenzaldehydes difficult. The above reaction takes place so readily that to obtain the condensation product it is merely necessary to mix the alcoholic solutions of the compounds and allow the mixture to stand at the temperature of the room over night.

Bamberger and Friedmann[4] obtained, by the action of zinc dust upon *m*-nitrobenzaldehyde, a substance of the formula $(C_7H_5ON)^x$, which is very insoluble in all ordinary organic solvents and which, when oxidized by ferric chloride, yields, *m*-nitrosobenzaldehyde. Gattermann,[5] by the electrolytic reduction of *p*-nitrobenzaldehyde and of *m*-nitrobenzaldehyde, dissolved in concentrated sulphuric acid, obtained the two isomeric N-formylphenyl ethers of the nitrobenzaldoximes. These compounds are insoluble in ordinary solvents but may be recrystallized from pyridine. Each, on oxidation, yields together with the nitrosobenzaldehyde a small amount of what has since been found to be the corresponding azoxybenzaldehyde.[6]

Kirpal,[7] using zinc dust as a reducing agent, tried to obtain the N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime. In this he was

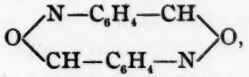
[1] *Ber. d. chem. Ges.*, **29**, 3037 (1896).
[2] *Ibid.*, **34**, 3877 (1901).
[3] *Ztschr. phys. Chem.*, **26**, 50.
[4] *Ber. d. chem. Ges.*, **28**, 250 (1895).
[5] *Ibid.*, **29**, 3037 (1896).
[6] *Am. Chem. J.*, **28**, 34.
[7] *Ber. d. chem. Ges.*, **30**, 1597 (1897).

not successful but obtained a yellow solution which on oxidation yielded *p*-nitrosobenzaldehyde.

Later, Kalle & Co.[1] patented a process for the preparation of aromatic hydroxylamine compounds by the treatment of nitro-compounds with zinc dust and an aqueous solution of an ammonium salt in the cold. It was stated that *p*-hydroxylaminobenzaldehyde, like various other hydroxylamine derivatives, was obtained by this method in quantitative yield. No details of the method and no description of the aldehyde were given. By this method phenylhydroxylamine may be obtained in almost quantitative yield but we were unable to obtain a satisfactory yield of the hydroxylaminobenzaldehyde.

Our knowledge of the hydroxylamino- and nitrosobenzaldehydes, may, accordingly, be summarized as follows: *m*-nitrobenzaldehyde and *p*-nitrobenzaldehyde, when subjected to electrolytic reduction in concentrated sulphuric acid solution, yield the corresponding N-formylphenyl ethers of the nitrobenzaldoximes, which, by oxidation with ferric chloride, give *m*-nitrosobenzaldehyde and *p*-nitrosobenzaldehyde. The same aldehydes when reduced by zinc dust form substances of unknown nature, which, by oxidation, yield nitrosobenzaldehydes identical with those mentioned above.

While we obtained various condensation products of the hydroxylaminobenzaldehydes neither of the above-mentioned insoluble ethers was detected among the reduction products. The insoluble compound obtained by Bamberger and Friedmann,[2] from *m*-nitrobenzaldehyde evidently has the formula,



and is not identical with the insoluble secondary product of electrolytic reduction as has been suggested.[3] *p*-Nitrobenzaldehyde forms a similar compound together with one or more insoluble condensation products of *p*-hydroxylaminobenzaldehyde.

EXPERIMENTAL.

Kirpal[4] boiled 200 cc. of water with 4 grams *p*-nitrobenzalde-

[1] D. R. P. 899,781: *Chem. Centrbl.*, **1**, 351 (1897).
[2] *Loc. cit.*
[3] *Ber. d. chem. Ges.*, **29**, 3037 (1896).
[4] *Loc. cit.*

hyde and 20 grams zinc dust for three minutes. A yellow solution was obtained, from which, by oxidation with ferric chloride solution, *p*-nitrosobenzaldehyde was obtained and from which, by the action of the air, *p*-azoxybenzaldehyde was formed. He was unable to isolate the hydroxylaminobenzaldehyde. Our repetition of Kirpal's work confirmed his results. The residue of zinc dust was colored slightly yellow. Attempts to extract this yellow substance with boiling water yielded *p*-azoxybenzaldehyde and a compound crystallizing in red needles and melting at 222° which has not been further investigated. By using benzene, instead of water, only *p*-azoxybenzaldehyde was obtained.

That these are decomposition products of the substance that colors the zinc dust yellow is evident from the fact that when covered with a great excess of ferric chloride solution and subjected to distillation with steam, *p*-nitrosobenzaldehyde was obtained. Neither of the two substances mentioned, when treated in the same manner, gave a nitroso-compound. That the nitroso-compound, in this case, does not result from the oxidation of the simple hydroxylaminobenzaldehyde may be seen from the following. The residue was treated with boiling alcohol and filtered. The filtrate was yellow in color. With ferric chloride it gave a very small quantity of *p*-nitrosobenzaldehyde, and when shaken with sodium hydroxide solution in contact with the air, *p*-azoxybenzaldehyde was formed. Using the same amount of alcohol in each case the extraction was repeated four times. Each of the solutions (except the last), so obtained, had the same color and gave the same oxidation products. The last was almost colorless and the zinc dust showed no trace of yellow. No *p*-nitrobenzaldehyde could be obtained from the oxidation products by recrystallizing them from glacial acetic acid.

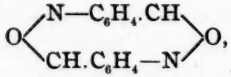
By using ammonium chloride the reduction product was obtained free from unchanged zinc. The latter, when present, seriously interferes with the investigation of the insoluble reduction product. A mixture of 10 grams *p*-nitrobenzaldehyde, 10 cc. alcohol, 30 cc. water and 10 cc. 2N ammonium chloride solution was warmed to 70°. Ten grams of zinc dust were added and the mixture violently agitated three to four minutes, keeping the temperature at 70°. The mixture became green, then yellow.

The whole was at once filtered under suction. The filtrate was light red in color and the residue yellow. The latter was extracted with 100 cc. boiling alcohol. The filtrate from this resembled the first except that the color was of a lighter shade. By the addition of water to these two filtrates we obtained a yellow crystalline substance, soluble in alcohol, ether, benzene and hot water. Aqueous alkalies imparted a deep red coloration to its aqueous and alcoholic solutions, from which the color slowly faded, *p*-azoxybenzaldehyde separating out. With ferric chloride solution it gave *p*-nitrosobenzaldehyde. It was unstable when exposed to the air in moist condition, various red and yellow compounds being formed. On account of the ease with which it underwent decomposition we failed to obtain it in pure condition from the limited amount of *p*-nitrobenzaldehyde that we had at our disposal. A nitrogen determination was made of a specimen obtained by recrystallizing the crude substance from absolute alcohol and drying the crystals at once. It melted at 98° to 101°. Calculated for $HO.NH.C_6H_4.CHO$, N = 10.2. Found, 10.1. It was evidently *p*-hydroxylaminobenzaldehyde,

$$C_6H_4\begin{cases}NH.OH\\CHO\end{cases}.$$

The yellow residue of zinc oxide remaining after the treatment with alcohol was extracted six times with boiling alcohol, using 100 cc. each time. All the filtrates so obtained, acted alike. All were yellow in color, gave no precipitate with water, gave *p*-nitrosobenzaldehyde with ferric chloride and *p*-azoxybenzaldehyde with aqueous alkalies. No *p*-nitrobenzaldehyde was obtained by the oxidation. The residue was still yellow in color. It was extracted twice with boiling benzene and the cooled filtrates treated with ligroin. The first gave a yellow precipitate, the second was colored yellow but gave no precipitate and on complete evaporation left only a trace of yellow solid. The residue of zinc dust was colored brown. It was extracted twice with boiling alcohol without any sign of the extraction being complete. Both of these filtrates were similar to the other alcoholic filtrates in color and reactions. The yellow compound precipitated from benzene by ligroin melted at 205° to 206° and was very sparingly

soluble in boiling alcohol, forming a yellow solution which gave the characteristic red coloration with aqueous alkalies, and yielded *p*-nitrosobenzaldehyde but no *p*-nitrobenzaldehyde when oxidized by ferric chloride. This compound, which was also obtained in small quantity by the action of amalgamated aluminum upon *p*-nitrobenzaldehyde in ethereal solution, has not been further investigated. The brown residue on oxidation yielded *p*-nitrosobenzaldehyde. It gave no *p*-nitrobenzaldehyde when covered with dilute sulphuric acid and treated with steam. The substance causing the brown color did not dissolve in boiling pyridine. It is evident from the above that there was, at most, no appreciable amount of the N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime among the reduction products. The yellow and brown substances were condensation products of *p*-hydroxylaminobenzaldehyde, the former being probably



which, when warmed with aqueous alcohol, changes partly into the simple hydroxylaminobenzaldehyde, according to the equation

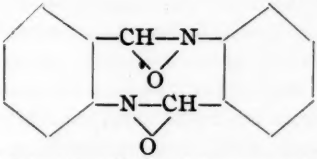
$$C_{14}H_{10}O_2N_2 + 2H_2O = 2C_7H_7O_2N.$$

If the mixture of *p*-nitrobenzaldehyde, alcohol, water and ammonium chloride solution be kept at 16° to 18° and the zinc dust added in small portions in the course of two hours, frequently shaking the mixture, the same compounds are obtained but the amount of the condensation products is less. If the mixture of all the compounds be made in the cold and left to itself the temperature rises until the liquid boils violently. The reaction product is brown in color and reacts in the same manner as the insoluble condensation product already described.

By the action of amalgamated aluminum upon the ethereal solution of *p*-nitrobenzaldehyde, similar condensation products were obtained.

m-Nitrobenzaldehyde, when treated in the same manner, yielded a brownish yellow solution from which *m*-nitrosobenzaldehyde and *m*-azoxybenzaldehyde were obtained by methods analogous to those used in the case of the para-compounds. Mixed with the zinc oxide and unchanged zinc was the gray substance, insoluble

in solvents, which Bamberger and Friedmann have found to have the formula $(C_7H_5ON)_x$. Analogous to the para-compound it gave a yellow solution when boiled with aqueous alcohol. The alcoholic solutions, so obtained, yielded small amounts of *m*-nitrosobenzaldehyde and *m*-azoxybenzaldehyde. The insoluble substance is probably the inner anhydride of *m*-hydroxylaminobenzaldehyde,



p-Nitrosobenzaldehyde.—When this compound is prepared by the oxidation of the N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime the yield varies from 10 to 15 per cent. of the weight of *p*-nitrobenzaldehyde reduced. It is much more readily obtained as follows: The red colored solution, described above, containing *p*-hydroxylaminobenzaldehyde is at once treated with an excess of 10 per cent. ferric chloride solution and allowed to stand for a few hours. The yellow *p*-nitrosobenzaldehyde gradually separates out. Steam is passed through the mixture, the nitroso compound being carried over. The yield varies from 15 to 20 per cent. of the weight of the nitrobenzaldehyde used. The yield may be increased by oxidizing the insoluble condensation products.

The liquid that collects in the receiver, when this compound is separated from the ferric chloride by distillation with steam, is deep green in color. On cooling, the color gradually disappears, the yellow nitroso-compound separating out. If this is filtered out and dried at a low temperature it sometimes shows a distinctly green tint. The filtrate, if the mixture has been allowed to stand long enough, is colorless. By recrystallizing the nitrosobenzaldehyde, from glacial acetic acid, yellow needles are obtained. When these are dried and boiled with water they do not dissolve, the liquid remaining colorless. If a current of steam be passed through the boiling mixture of water and *p*-nitrosobenzaldehyde, the same result is not always observed. Sometimes no nitroso-compound is carried over with the steam, while at other times it passes over very slowly, collecting in the receiver as a green solu-

tion from which, on cooling, very little nitrosobenzaldehyde separates. In one experiment in which the distillate was colorless after steam had been passed through the mixture for some time, finely divided calcium chloride was added in small portions, a burner being kept under the distilling flask. When the temperature in the latter had thus been raised to 130° the *p*-nitrosobenzaldehyde floated unchanged on the surface of the liquid. The addition of the next portion of calcium chloride, which raised the temperature to 140°, caused the nitroso-compound to pass over very rapidly. Very impure specimens of the nitrosoaldehyde were purified by adding them to this calcium chloride solution which was kept at the boiling-point while steam was passed through. When the mixture of water and *p*-nitrosobenzaldehyde collecting in the receiver in the preparation of the latter is divided into two portions and the one immediately subjected to the action of a current of steam while the other is allowed to stand ten or twelve hours before undergoing similar treatment, a marked difference is to be noticed. In the case of the first the nitrosobenzaldehyde passes over rapidly but in the second very slowly. It dissolves in hot solvents, as acetic acid, alcohol and acetone with a deep green color. As these cool, the color slowly changes to yellow with or without separation of crystals. While the green color usually disappears within a few hours it sometimes remains for several days. As *p*-nitrosobenzaldehyde melts at 137° it would necessarily pass into the green or monomolecular condition when brought into contact with the calcium chloride solution boiling at 140°.

m-Nitrosobenzaldehyde, unlike the isomeric para-compound, is colorless in the solid state, distils readily with steam and dissolves in cold solvents with a deep green color.

UNIVERSITY PLACE, NEB.,
June 20, 1902.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NEBRASKA WESLEYAN UNIVERSITY.]

ON THE NITRATION OF BENZYL CHLORIDE.

BY FREDERICK J. ALWAY.

Received July 21, 1902.

WHILE the three nitrobenzyl chlorides are well-known compounds and the action of fuming nitric acid upon benzyl chloride

has been described by different investigators, no definite information has been furnished as to the yield of *p*-nitrobenzyl chloride obtained at different temperatures. There is, also, little agreement as to the nature of the oily by-product.

Beilstein and Geitner[1] were the first to obtain *p*-nitrobenzyl chloride from benzyl chloride. Grimaux[2] repeated their work. Strakosch[3] improved the method by keeping the temperature at —15° during the operation. The later investigators, Abelli,[4] Nölting[5] and Klumpf,[6] followed the method of Strakosch. As attempts made in this laboratory to verify the statement of Strakosch, that very little except *p*-nitrobenzyl chloride is obtained at the above-mentioned temperature and that the oily by-product consists essentially of unchanged benzyl chloride, were unsuccessful, various nitration methods were tried in order to determine the conditions under which the maximum yield of *p*-nitrobenzyl chloride is obtained. It was found that the yield of *p*-nitrobenzyl chloride under the most favorable conditions, was 50 per cent. of the theoretical and that the oily by-product obtained by the different methods consists of nitrobenzyl chlorides, in some cases mixed with dinitrobenzyl chloride. If a mixture of slightly more than the theoretical amount of fuming nitric acid with concentrated sulphuric acid be added to cooled benzyl chloride a very low temperature is not required to ensure the maximum yield. If a considerable excess of fuming nitric acid be used, dinitrobenzyl chloride is formed. Ordinary concentrated nitric acid may be used instead of the fuming acid, the yield of *p*-nitrobenzyl chloride, however, being less.

EXPERIMENTAL.

The crude nitration product obtained in each of the cases described below, was added to a mixture of ice and water. The more or less pasty solid, so obtained, was transferred to a Büchner funnel and subjected to powerful filtration until oily drops ceased to pass through. The residue, when recrystallized

[1] *Ann. Chem.* (Liebig), **139**, 337 (1866).
[2] *Ibid.*, **145**, 46 (1868).
[3] *Ber. d. chem. Ges.*, **6**, 1059 (1873).
[4] *Ibid.*, **16**, 1232; *Gazz. chim. ital.*, **13**, 97 (1883).
[5] *Ber. d. chem. Ges.*, **17**, 385 (1884).
[6] *Ann. Chem.* (Liebig), **224**, 96 (1884).

from alcohol, gave pure *p*-nitrobenzyl chloride. By treating the mother-liquor with water a further yield was obtained. In estimating the yield of solid and liquid nitration products, the residue, without further treatment, was weighed, while the liquid was washed with water, separated and dried before weighing.

Three hundred grams of fuming nitric acid (sp. gr. 1.5) were placed in a flask surrounded by a mixture of ice and salt. Benzyl chloride was added drop by drop. As each drop came in contact with the acid a reddish brown coloration was produced. At first this coloration quickly disappeared but as the addition of benzyl chloride proceeded the color disappeared more and more slowly until, after 120 grams of benzyl chloride had been added, it remained. During the operation the temperature was kept at —15° to —13°. Yield of solid, 85 grams; of liquid, 85 grams. Time required, two hours and thirty minutes. The yield of the two products was the same when the temperature was kept at —25°, as well as when fuming nitric acid was added to benzyl chloride kept at —15°. At 20° to 30° the yield of the solid was only half so great and of liquid half as great again.

The following was found to be the most satisfactory method of obtaining *p*-nitrobenzyl chloride. A mixture of 90 grams fuming nitric acid and 180 grams concentrated sulphuric acid was added to 120 grams benzyl chloride, kept at —5° to —10°. After about half the acid mixture had been added, white crystals began to separate. At the end of the operation the contents of the flask were almost solid. Yield of solid, 85 grams; of liquid, 87 grams. Time required one hour and ten minutes. At temperatures above 0° the yield was less.

To determine the action of a considerable excess of fuming nitric acid, 40 grams of benzyl chloride were added to a mixture of fuming nitric acid (80 grams) and concentrated sulphuric acid (180 grams). The temperature was kept below 40°. After being allowed to stand two hours the mixture was poured into ice water. An oily liquid separated. This passed through the filter, leaving no residue. It was washed well with water, dried with calcium chloride, filtered and analyzed. It consisted essentially of one or more dinitrobenzyl chlorides.

The specific gravity and the nitrogen content were determined

in the case of each of the oily liquids obtained by the above methods.

	Calculated for $NO_2.C_6H_4.CH_2Cl$.	Calculated for $(NO_2)_2C_6H_3.CH_2Cl$.	Found. I.	II.	III.
Nitrogen.....	8.2	12.9	8.7	8.6	12.1
Specific gravity at 27°		..	1.333	1.332	1.476

From the above it is evident that not only is the yield of *p*-nitrobenzyl chloride practically the same but that the by-products are also the same, whichever of the two methods of preparing *p*-nitrobenzyl chloride is employed. The further investigation of the dinitrobenzyl chloride was not proceeded with as Cohn and Friedlander[1] have recently obtained *o*-*p*-dinitrobenzyl chloride by an analogous method and have announced their intention of soon publishing the details of their work.

UNIVERSITY PLACE, NEB.,
June 16, 1902.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA].

CONDENSATION OF CHLORAL WITH THE NITRANILINES.

BY ALVIN S. WHEELER AND H. R. WELLER.

Received July 28, 1902.

CHLORAL forms condensation products readily with aromatic amines according to the equation

$$CCl_3CHO + 2RNH_2 = CCl_3CH(NHR)_2 + H_2O.$$

O. Wallach[2] effected the condensation of chloral with aniline, the product being trichlorethylidenediphenylamine,

$$CCl_3CH(NHC_6H_5)_2.$$

In 1898 Eibner[3] and Baskerville, working independently, carried out the condensation of chloral with *p*-nitraniline. Baskerville's results are incorporated in the present paper. Our investigation shows that similar products are obtained with ortho- and meta-nitraniline. The melting-points of the condensation products form an ascending series as in the nitranilines. The chloral used was prepared by distilling chloral hydrate with concentrated sulphuric acid and the nitranilines were recrystallized until pure.

Trichlorethylidenedi-o-nitrophenamine,

[1] *Ber. d. chem. Ges.*, **35**, 1266 (1902).
[2] *Ann. Chem.* (Liebig), **173**, 278.
[3] *Ibid.*, **302**, 366.

$CCl_3CH(NHNO_2C_6H_4)_2$.—Five grams of *o*-nitraniline were suspended in 75 cc. of benzene and 5 grams of chloral were added. Two and one-half grams of chloral are required by theory. The crystalline nitraniline was quickly converted into a flocculent precipitate which melted at 162°. The benzene solution was evaporated down to a gummy mass on the water-bath, the residue was taken up with boiling alcohol and, upon cooling, a beautiful yellow crystalline precipitate settled out. The two precipitates were recrystallized from hot alcohol until the melting-point was raised to 171°. A determination of chlorine gave 26.10 per cent. Calculated for $C_{14}H_{11}O_4N_4Cl_3$, 26.22 per cent.

Trichlorethylidenedi-*o*-nitrophenamine crystallizes from hot alcohol in yellow transparent rectangular plates and melts at 171°. It is insoluble in ether and ligroin but soluble in acetone, chloroform and benzene. It may be purified by dissolving in glacial acetic acid and precipitating with water. It is not decomposed by water and is insoluble in hot hydrochloric acid. The yield was about 45 per cent. of the theory.

Trichlorethylidenedi-m-nitrophenamine, $CCl_3CH(NHNO_2C_6H_4)_2$.—Five grams of *m*-nitraniline were suspended in 125 cc. benzene and 5 grams of chloral were added. The needle crystals of *m*-nitraniline were quickly converted into a flocculent precipitate, at first yellowish white but soon assuming a rich flesh color which was permanent. The crude substance decomposed at 208°. On digestion with acetone the impurities were dissolved out and the melting-point was raised to 212°. A determination of chlorine gave 26.18 per cent. Theory requires 26.22 per cent.

Trichlorethylidenedi-*m*-nitrophenamine crystallizes from alcohol in rectangular plates of a rich flesh color. It melts at 212°. It is readily soluble in alcohol and insoluble in ether, ligroin and benzene. It is decomposed by hot water and by hydrochloric acid, chloral and *m*-nitraniline being re-formed. The yield of the condensation product is about 30 per cent of the theory.

The reaction seems to run a different course if the materials are boiled for some time under a reflux condenser. Under these circumstances a body is obtained which, upon recrystalling once from alcohol, melts at 89°. A single analysis for chlorine showed

the presence of 32.3 per cent. This substance will be examined further.

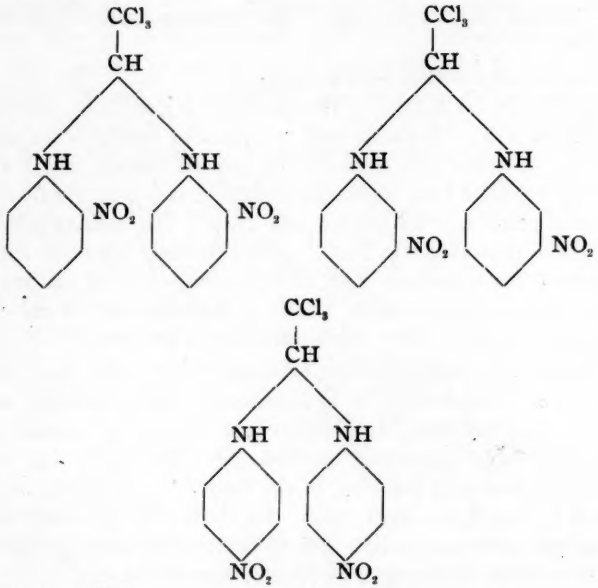
Trichlorethylidenedi-p-nitrophenamine, $CCl_3CH(NHNO_2C_6H_4)_2$.—Ten grams of *p*-nitraniline were suspended in 100 cc. benzene, and 15 grams of chloral were added slowly. A heavy yellow precipitate formed immediately. After heating for some time on the water-bath to complete the reaction, the precipitate was filtered off and dried. The melting-point of the crude substance was 210°. It is extremely insoluble and by removing the impurities with small amounts of cold acetone the melting-point was raised to 216°. A determination of the chlorine gave 26.35 per cent. Calculated, 26.22 per cent.

Trichlorethylidenedi-*p*-nitrophenamine is a yellow powder of very great insolubility. It is insoluble in water, alcohol, ether, ligroin and benzene. It is somewhat soluble in acetone and readily soluble in boiling nitrobenzene. The yield was 14.51 grams or nearly 54 per cent. of the theory. It is slowly decomposed by hot hydrochloric acid. Its conversion by acetic anhydride into *p*-nitroacetanilide and by benzoyl chloride into benzoyl *p*-nitroanilide, asdescribed by Eibner, was carried out.

Reduction of the Nitroamines.—We have tried to reduce these nitroamines with various reducing agents but so far without success. If the nitro-group could be reduced, the resulting amine might again react with chloral, forming a complex ring body. Interesting results were obtained when the nitroamines were boiled with ammonium sulphide in alcoholic solution. In each case a volatile substance condensed on the walls of the reflux air condenser in white crystals. In the case of the para-compound, these crystals melted at 120° and were insoluble in water and alcohol, but dissolved readily in carbon disulphide. This group of bodies will be studied further in this laboratory.

In naming these compounds Eibner places the "di" after the "nitro" but it seems preferable to us to place it before the "*p*".

Constitution.—In the reaction between chloral and the nitranilines it might be possible for the oxygen to combine with hydrogen in the ring, leaving the amino groups untouched. But these substances do not possess any basic properties; hence they are to be represented as follows:



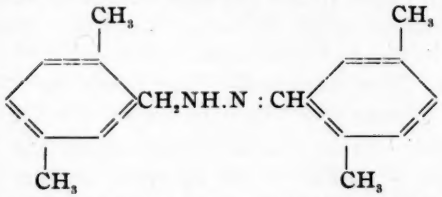
CHAPEL HILL, N. C.,
July 24, 1902.

PREPARATION OF 2,5-DIMETHYLBENZYL-2,5-DIMETHYLBENZAL HYDRAZONE AND ITS BENZOYL AND ACETYL DERIVATIVES.

BY EVERHART PERCY HARDING AND EDGAR W. RICE.

Received August 11, 1902.

2,5-Dimethylbenzyl-2,5-dimethylbenzal Hydrazone,



To an alcoholic solution of 2,5-dimethylbenzaldazine, prepared according to Curtius and Jay,[1] was added more than the calculated

[1] *J. prakt. Chem.*, **89**, 43.

amount of a 4 per cent. sodium amalgam sufficient to reduce the aldazine to its corresponding hydrazone. This was heated in a flask connected with a reflux condenser for from three to four hours upon a water-bath. The solution, nearly colorless, was then filtered and the filtrate left in a freezing-mixture of salt, ice and water until the hydrazone crystallized out. The hydrazone was then filtered off, washed with water and recrystallized from alcohol. It melted at 74°-78° (uncorr). The reaction takes place according to the following equation:

$$(CH_3)_2C_6H_3CH : N.N : CH.C_6H_3(CH_3)_2 + H_2 =$$
$$(CH_3)_2C_6H_3CH_2.NH.N : CH.C_6H_3(CH_3)_2.$$

The analysis gave: C, 81.03; H, 8.21. Calculated: C, 81.2; H, 8.04.

2,5-Dimethylbenzyl-2,5-dimethylbenzal hydrazone is soluble in ether, chloroform, benzene, carbon bisulphide, toluene, ethyl alcohol, methyl and amyl alcohols. It is insoluble in water. The hydrazone is very unstable and begins to decompose at once when exposed to the air.

Acetyl 2,5-dimethylbenzyl-2,5-dimethylbenzal Hydrazone,

$$(CH_3)_2C_6H_3CH_2N(C_2H_3O)N : CHC_6H_3(CH_3)_2.$$

To a concentrated alcoholic solution of the hydrazone was added a slight excess of acetic anhydride and the solution evaporated slowly to dryness upon a water-bath. The residue was recrystallized from alcohol. It gave long, white, satin-like needles which melted at 137°.

The analysis gave 9.11 per cent. N. Calculated, 9.09 per cent.

The acetyl derivative is soluble in benzene, toluene, ether, chloroform, carbon disulphide, acetic acid and in hot ethyl, methyl, and amyl alcohols. It is insoluble in water.

Benzoyl 2,5-dimethylbenzyl-2,5-dimethylbenzal Hydrazone,

$$(CH_3)_2C_6H_3CH_2N(C_6H_5CO)N : CHC_6H_3(CH_3)_2.$$

A slight excess of benzoyl chloride was added to a concentrated alcoholic solution of the hydrazone and the solution evaporated to dryness upon a water-bath. The residue was recrystallized from alcohol. Long satin-like crystals formed which melted at 134°-134.5°.

The analysis gave 7.60 per cent. N. Calculated, 7.57 per cent.

The benzoyl derivative is soluble in benzene, toluene, ether,

chloroform, carbon disulphide, acetic acid and in hot ethyl, methyl, and amyl alcohols. It is insoluble in water.

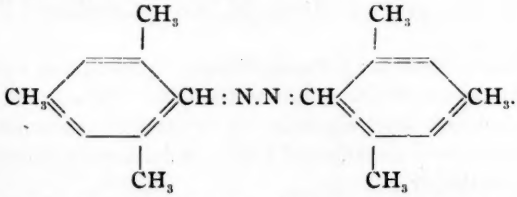
Nitroso and picric acid derivatives are at present being prepared.

PREPARATION OF 2,4,6-TRIMETHYLBENZALDAZINE; OF 2,4,6-TRIMETHYLBENZYL-2,4,6-TRIMETHYLBENZAL HYDRAZONE AND SOME OF ITS DERIVATIVES.

By Everhart Percy Harding.

Received August 11, 1902.

2,4,6-Trimethylbenzaldazine,



2,4,6-Trimethylbenzaldazine was prepared by adding to a weak alcoholic solution of 2,4,6-trimethylbenzaldehyde, which was prepared according to Gattermann,[1] a solution of hydrazine sulphate containing the calculated amount of sulphate to produce the corresponding aldazine. The mixed solutions were warmed to 60°, violently shaken for thirty minutes and allowed to stand for two hours. The yellow substance that separated formed spherulitic masses which recrystallized from acetic acid in beautiful light yellow prisms which melted at 167°.

$$(CH_3)_3C_6H_2CHO + H_2N'NH_2 + OHCC_6H_2(CH_3)_3 =$$
$$(CH_3)_3C_6H_2.CH : N.N : CH.C_6H_2(CH_3)_3.$$

These gave 9.59 per cent. N. Calculated, 9.56 per cent.

2,4,6-Trimethylbenzaldazine is very soluble in chloroform. It is soluble in cold ether, benzene, toluene, acetone and in hot acetic acid, ethyl, methyl and amyl alcohols. It is insoluble in water. Like all known aldazines it is a very stable compound.

2,4,6-Trimethylbenzyl-2,4,6-trimethylbenzal Hydrazone,

$$(CH_3)_3C_6H_2CH_2NHN : CHC_6H_2(CH_3)_3.$$

More than the calculated amount of a 4 per cent. sodium amalgam

[1] W. Graf: Inaug. Diss., Heidelberg, 1899.

to reduce the aldazine to its corresponding hydrazone was added to an alcoholic solution of 2,4,6-trimethylbenzaldazine. This was heated at the temperature of boiling alcohol in a flask connected with a reflux condenser for from four to five hours upon a water-bath. The almost colorless solution was then filtered and the filtrate placed in ice water. The hydrazone crystallized at once. It was filtered off, washed well with water and recrystallized from alcohol. It melted at 88°-89° (uncorr.).

The analysis gave 9.40 per cent. N. Calculated, 9.53 per cent.

2,4,6-Trimethylbenzyl-2,4,6-trimethylbenzal hydrazone is very soluble in ether and benzene, less soluble in acetic acid, ethyl and methyl alcohols and insoluble in water. It is very unstable, decomposing at once when exposed to the air and after a short time in an exhausted desiccator.

Acetyl 2,4,6-Dimethylbenzyl-2,4,6-trimethylbenzal Hydrazone,

$$(CH_3)_3C_6H_2CH_2N(C_2H_3O)N : CHC_6H_2(CH_3)_3.$$

To a concentrated alcoholic solution of the hydrazone was added acetic anhydride in excess and the solution evaporated slowly to dryness upon a water-bath. The residue was recrystallized from alcohol. Long, satin-like, white needles were formed which melted at 155°.

The analysis gave 8.42 per cent. N. Calculated, 8.34 per cent.

Acetyl 2,4,6-trimethylbenzyl-2,4,6,trimethylbenzal hydrazone is very soluble in chloroform, ether, benzene, toluene, acetic acid and acetone. It is less soluble in ethyl, methyl and amyl alcohols and insoluble in water. It is a very stable compound.

Benzoyl 2,4,6-Trimethylbenzyl-2,4,6-trimethylbenzal Hydrazone,

$$(CH_3)_3C_6H_2CH_2N(C_7H_5O)N : CHC_6H_2(CH_3)_3.$$

A slight excess of benzoyl chloride was added to a concentrated alcoholic solution of the hydrazone and the solution evaporated to dryness upon a water-bath. The residue was taken up and recrystallized from alcohol. Long, satin-like needles were formed which melted at 142.5°-143°.

The analysis gave 7.03 per cent. N. Calculated, 7.23 per cent.

The benzoyl derivative is very soluble in chloroform, ether, toluene, acetone, benzene and acetic acid. It is less soluble in ethyl, methyl, and amyl alcohols, and is insoluble in water. It is a very stable compound.

Nitroso 2,4,6-Trimethylbenzyl-2,4,6-trimethylbenzal Hydrazone,

$(CH_3)_3C_6H_2CH_2N(NO)N : CHC_6H_2(CH_3)_3$.

To a strong alcoholic solution of 2,4,6-trimethylbenzyl-2,4,6-trimethylbenzal hydrazone, cooled by ice water, was added a few drops of concentrated hydrochloric acid. To this cold solution, which was shaken after each addition, was added gradually a concentrated solution of sodium nitrite. Long, satin-like needles separated at once and increased in number upon the addition of water. The successful carrying-out of this experiment requires the use of freshly prepared hydrazone.

The nitroso derivative was filtered off, washed well with water to remove the excess of sodium nitrite, and recrystallized from alcohol. The long, yellow, satin-like crystals melted at 117°.

The analysis gave 13.09 per cent. N. Calculated, 13.00 per cent.

The nitroso derivative is very soluble in chloroform, ether, benzene, and toluene. It is less soluble in acetone and glacial acetic acid. It is soluble in warm ethyl, methyl, and amyl alcohols, and insoluble in water. It is a stable compound.

UNIVERSITY OF MINNESOTA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

ARSENIC PENTACHLORIDE.

BY CHARLES BASKERVILLE AND H. H. BENNETT.

Received June 13, 1902.

THE non-existence of arsenic pentachloride has for a long time been regarded as remarkable, especially so when the analogues of that element having atomic weights below and above it, phosphorus and antimony, show pentavalence toward the halogens.

Hurtzig and Geuther[1] endeavored to prepare it by treating arsenious acid with phosphorus pentachloride. Mayerhofer[2] passed chlorine into arsenic trichloride at —10° C., removing the excess of chlorine by a stream of carbon dioxide, and failed to obtain the body. Janovsky[3] treated phosphorus pentachloride with arsenic trihydride at 0° C. with negative results. Dumas[4]

[1] *Ann. Chem. Pharm.*, **111**, 171.
[2] *Ibid.*, **158**, 326.
[3] *Ber. d. chem. Ges.*, **8**, 1636 (1875).
[4] *Ann. Chem.* (Liebig), **33**, 337.

thought he had arsenic pentachloride, but Capitaine[1] proved it to be a mixture of As_4O_6 and $AsCl_3$. Weber having prepared $SbCl_5PCl_5$, Cronander[2] sought its analogue $AsCl_5PCl_5$, but only obtained $AsCl_3PCl_5$. Marignac[3] obtained AsF_5 as a double fluoride of potassium. Sloane[4] prepared AsI_5 and endeavored to secure the pentachloride by saturating arsenic trichloride with chlorine at —23° C. at ordinary pressure and obtained the ratio As : Cl :: 1 : 4.447. There was a gradual decrease in the ratio up to 24° C. when it became 1 : 4.08, then there was an abrupt change rapidly approaching 1 : 3. Such observations made the existence of As_2Cl_8 quite conceivable.

Baeyer's pentahalogen compounds of arsenic in which one to four chlorine atoms have been replaced by alkyl radicals and Michaelis'[5] work with phenyl residues are well known. Recently the pentavalent organic arsenic compounds have become much augmented by the extensive work of Michaelis.[6]

The procedure of Sloane[7] offered encouragement, provided the reaction should be carried out at a lower temperature. Chemically pure arsenic trichloride was prepared and redistilled from concentrated sulphuric acid and its purity determined by analysis. About 5 cc. of the liquid were placed in a dry test-tube buried in solid carbon dioxide loosely packed in a Dewar bulb and dry chlorine led in. The crystalline trichloride (m. p. —18° C.) assumed a greenish yellow color and became liquid, which grew in bulk. Besson[8] showed that arsenic trichloride saturated with chlorine at zero does not solidify at —30° C. Davy also showed that it does not freeze at —29° C. when well saturated with chlorine. After a few minutes, the time varying with different experiments, the stream of gas was cut off and the excess of liquid chlorine removed by fractional distillation. Chlorine boils at —33.6° C. We verified this by completely boiling away several cubic centimeters of chlorine at —33° C. in other experiments. As a safeguard we allowed the temperature to rise to —31° C.

[1] *Jour. Pharm.*, **25**, 524.
[2] *Ber. d. chem. Ges.*, **3**, 1466 (1873).
[3] *Ann. Chem.* (Liebig), **145**, 249.
[4] *Chem. News*, **46**, 194 (1881).
[5] *Ber. d. chem. Ges.*, **8**, 1316 and **9**, 1566.
[6] *Ann. Chem.* (Liebig), **320**, 271 (1902).
[7] *Loc. cit.*
[8] *Compt. rend.*, **109**, 940.

The liquid was cooled again to —35° C. and samples were removed as the temperature rose by means of a small pipette chilled to the temperature of the refrigerating agent. These samples in one experiment were placed directly in water; in another it was deemed better to place them in a dilute sodium hydroxide solution. In the former case immediate solution occurred with those portions removed at temperatures below —25° C., while at those higher a white precipitate, evidently of arsenious oxide, formed, increasing in amount with elevation of temperature. The orthoarsenic acid was determined as magnesium pyroarsenate and chlorine as silver chloride. The filtrate from the magnesium ammonium arsenate in the former was tested for the presence of arsenious compounds. None were found up to —25° C., when arsenious acid was found in traces increasing in amount with rise of temperature. The ratio between arsenic as arsenic acid, and chlorine, was 1:5 or $AsCl_5$. At —25° C. the ratio rose to 1:6. The loss of chlorine and consequent return to the trivalent condition became more and more marked, the higher the temperature.

The following analytical results were obtained for two temperatures in one experiment:

Temperature. °C.	Amount taken.	Chlorine found. Per cent.	Theoretical.	Ratio obtained. As : Cl.
—35	0.1796	69.93	70.26	1 : 4.93
—25	0.26675	73.21	....	1 : 5.78

Arsenic pentachloride is readily soluble in carbon disulphide and absolute ether cooled to —30° C. From the latter, when chilled several degrees, it crystallizes in yellow prisms. It loses chlorine when heated above —28° C. On exposure to the air it fumes, evolving hydrochloric acid vapor and as the temperature rises forms crystals, most likely of the trichloride, which melt soon to the liquid state. A special preparation was made and sealed in a tube. The greenish-yellow liquid when cooled to —38° or —40° C. (we had no thermometer for determining this accurately) formed beautiful yellow crystals.

It is not regarded necessary to give our several unsuccessful preliminary experiments to secure the body for analysis. Suffice it to say that placing the body in a pipette or weighing-bottle at the temperature of the air brought about its immediate decomposition to the original trichloride, chlorine being evolved.

UNIVERSITY OF NORTH CAROLINA,
April 15, 1902.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 66.]

OBSERVATIONS ON THE ELECTROLYTIC PRECIPITATION OF ZINC AND OF COPPER.

BY EDGAR F. SMITH.

Received July 3, 1902.

THE suggestions made for the electrolytic determination of zinc are numerous. During the last few months the writer has had occasion to have some of them tried with the view of fixing the most advantageous working conditions, and in the course of this inquiry has noted what appears to him to be a matter of some analytical interest, *viz.*, that by employing as electrolyte a zinc salt solution containing an alkaline acetate very satisfactory results are obtainable in a comparatively brief period. It was Riché who first proposed this electrolyte, but it has not met with general use, perhaps because the proper working conditions were lacking. These are given in this communication. They have been repeatedly employed by different persons in this laboratory and have proved to be trustworthy. It was thought advisable, in the determinations made, to use as cathodes platinum dishes, upon the inner surface of which there was deposited a silver coating instead of one of copper.

WORKING CONDITIONS.

Potassium zinc sulphate	0.2002 gr. Zn.
Sodium acetate	1 gram.
Acetic acid (99 per cent.)	0.3 cc.
Total dilution	150 cc.
Cathode surface	100 sq. cm.
$N.D._{100}$	0.36–0.70 ampere.
Voltage	4–5.
Temperature	65° C.
Time	2 hours.

A flat platinum spiral was used as anode. The solution was heated to the required temperature before the current was passed through it. At the beginning the pressure equaled four volts. This was maintained for an hour when it was increased to five volts, with the corresponding rise in amperage. On exposing a clean silver surface, if there was no further deposition of zinc and the liquid showed an acid reaction, a few drops of ammonia water were added to the point of neutralization and the action of the

current continued for about fifty minutes longer, after which a portion of the liquid was tested for zinc by the ferrocyanide method.

It will usually be noticed after an hour's action that the solution seems to be filled with bubbles. This is the proper time to introduce the ammonia water for neutralization. When the metal has been fully precipitated the liquid should be siphoned off, and the zinc deposit be washed with water, alcohol and ether. It may then be dried and weighed. By this procedure these results were obtained:

Zinc potassium sulphate. Grams.	Zinc found. Gram.	Zinc required. Gram.
1.3598	0.2006	0.2002
1.3580	0.1997	0.2000
1.2621	0.1806	0.1862
1.2742	0.1879	0.1883

The deposits of metal were all very adherent, free from sponginess and light gray in color.

Very often questions are asked regarding the availability of electrolytic methods in determining the quantities of metals in technical products. The idea seems to exist that these methods may be satisfactory enough and yield good results so long as pure salts or mixtures of the same are used, but that equal success will probably not be reached if natural products are used. Perhaps it would be well to try all proposed methods in this particular. The writer has no doubt in his own mind as to the outcome. It will be wholly satisfactory. Believing this he had several samples of zinc blende decomposed rapidly with acid, the solutions evaporated to dryness, the residues taken up in water and a drop or two of sulphuric acid, when the liquids were filtered and mixed with sodium acetate and a little free acetic acid, after which they were electrolyzed with conditions like those previously recorded. The results were as follows:

Zinc blende. Gram.	Zinc found. Gram.	Zinc. Per cent.
0.2523	0.1681	66.62
0.2497	0.1662	66.56

These values agree closely with those obtained by the ordinary gravimetric methods, but it need scarcely be mentioned that the

time-factor is very greatly reduced, so that this procedure will recommend itself. The point might be raised that blendes frequently contain iron; will it not contaminate the zinc? Such was not observed to be the case in any of the many determinations conducted in this way. Probably, if the quantity of iron present should be large there might serious doubt arise, but in all instances of that kind as the acetate solution is heated before the current is allowed to act, the basic iron acetate would appear, could be filtered out, and the solution then be treated as previously directed. The method surely deserves a thorough trial at the hands of analysts.

In this connection it may not be out of place to call attention to copper determinations in chalcopyrite made in the electrolytic way. This again is a natural product and with those who have felt uncertain how the copper determination by means of the current would result, it has been customary, after decomposition of the mineral, to precipitate the copper as sulphide, then dissolve it in nitric acid or in potassium cyanide and electrolyze. This is not necessary. After the mineral is decomposed, paying no attention to the sulphur, evaporate to dryness, take up the residue with a little sulphuric acid and water, and then proceed with the electrolysis, using such conditions as these:

Total dilution	150 cc.
Concentrated sulphuric acid	10 cc.
Temperature	60°–70°.
$N.D._{100}$	0.8–1.0 ampere.
Volts	2–3.
Time	1 hour, 30 minutes.

RESULTS.

Chalcopyrite. Gram.	Copper found. Gram.	Copper. Per cent.
0.2900	0.0963	33.20
0.2900	0.0969	33.41
0.5800	0.1932	33.31
0.5800	0.1936	33.37
0.5800	0.1936	33.37

The liquid siphoned off from the deposit of copper may be nearly neutralized with ammonia water and, after the introduction of ammonium oxalate, be electrolyzed at a temperature of 40°-65°, with a current of $N.D._{100} = 0.5$-1.0 ampere and 2-3.5 volts.

RESULTS.

Chalcopyrite. Gram.	Iron. Gram.	Iron. Per cent.
0.5800	0.1746	30.10
0.5800	0.1750	30.17

The question has been asked whether it is not possible, in a case like that of chalcopyrite, to render the original solution of the mineral ammoniacal and, not regarding the precipitated ferric hydrate, proceed with the electrolytic deposition of the copper. Many have felt that there was danger of iron entering into the deposit of copper, while others have declared that such a condition was not to be feared. During the past winter numerous tests of this question have been made in this laboratory, working with chalcopyrite. It has been found that if platinum dishes be employed as cathodes to receive the copper, the latter has invariably been contaminated with iron, but that if platinum cylinders, dipping into the ammoniacal solution contained in beaker-glasses, were used for cathodes the copper deposited upon them was free from iron.

The writer has had the assistance of Messrs. J. H. Graham and F. E. Walker in the experimental part of this study and would here acknowledge his indebtedness to them.

UNIVERSITY OF PENNSYLVANIA.

THE USE OF POTASSIUM-FERRIC CHLORIDE FOR THE SOLUTION OF STEEL IN MAKING THE DETERMINATION OF CARBON.

BY GEO. WM. SARGENT.

Received July 27, 1902.

THE reaction considered to take place when steel or iron drillings dissolve in potassium-cupric chloride is expressed thus:

$$Fe + CuCl_2 = FeCl_2 + Cu \text{ and } Cu + CuCl_2 = Cu_2Cl_2.$$

This result expressed without indicating the intermediate reaction is written as follows:

$$Fe + 2CuCl_2 = FeCl_2 + Cu_2Cl_2.$$

The solution takes place more quickly and without any loss of carbon if hydrochloric acid (sp. gr. 1.2) is present in the ratio of 1 cc. to 13 cc. of the double chloride solution. The above equations do not contain the potassium chloride since the part enacted

by it is not clearly understood; without it the drillings dissolve very much more slowly.

If instead of the copper salt, potassium-ferric chloride be used with just sufficient free hydrochloric acid present to prevent the separation of any basic iron salt, the drillings will be found to go into solution just as quickly and with no loss of carbon. The iron salt has the formula $FeCl_3,2KCl,H_2O$ and may be prepared by adding to a ferric chloride solution the requisite amount of potassium chloride and crystallizing out the double salt.

The chemically pure ferric chloride of commerce has the following composition:

	Per cent.
Ferric chloride	51.55
Hydrochloric acid	0.65
Water	48.80

If then to 267 grams of this commercial ferric chloride, 130.7 grams of potassium chloride are added and the whole, when dissolved in water, made up to 1 liter in volume, the resulting solution will be equivalent to the potassium-cupric chloride solution as usually prepared, except that it will contain free hydrochloric acid in the ratio of but 1 cc. to 225 cc. This amount is sufficient to prevent the formation of any basic salt and if this amount be much exceeded the acid will attack the drillings, giving off hydrogen and hydrocarbons. The reaction that takes place using the iron salt is analogous to that when the copper salt is used, leaving out of course the intermediate reaction, and is indicated by this equation:

$$Fe + 2FeCl_3 = 3FeCl_2.$$

If the solution is found to attack the drillings with evolution of hydrogen, the free hydrochloric acid must be neutralized until sufficient is left to just prevent the formation of basic salts of iron. The liquid should be a beautiful amber color when the conditions are perfect. As the drillings dissolve, the color becomes darker and of a greenish cast yet transparent so that when the solution of the drillings is complete, can more readily be ascertained than is the case when the copper salt is the solvent. The filtrate from the carbon is quite transparent, consequently whether the filtering medium has been a perfect one or not is quickly seen without the dilution of the filtrate as is required when potassium-cupric chloride is the decomposing agent.

This filtrate before it is contaminated with any wash-water, may be chlorinated and used again for the solution of a second lot of drillings. In this way, by chlorinating,[1] the filtrate from the carbon is made to decompose the next sample of drillings. When sufficient iron chloride has accumulated, add more potassium chloride and water to make the solution of the original strength. To illustrate, 200 cc. of the solution of $FeCl_3$,2KCl containing about 50 grams of iron per liter are used in the decomposition of each factor weight, *2.7272* grams, of drillings. The liter will then contain besides the original amount 13.636 grams of iron. By chlorinating, four lots of 13.636 grams each or 54+ grams of iron may be dissolved in this liter. If 130.7 grams of potassium chloride be now added, the liter may be made two liters in volume. This operation of chlorinating, adding potassium chloride and diluting, may be carried on *ad infinitem.* It is, however, necessary at some point, determined by the amount of work done in the laboratory, to throw out a part of the accumulated solution.

In this way the waste product is utilized to assist in the next carbon determination and the expense materially reduced.

A table of results obtained by using both salts for the decomposition of the steels is appended.

Sample.	Dissolved in $CuCl_2$,2KCl. Per cent. carbon.	Dissolved in $FeCl_3$,2KCl. Per cent. carbon.
Standard 0.97 per cent	0.972	0.970
" 0.97 "	0.978	0.975
" 0.97 "	0.974	0.971
" 0.97 "	0.970	0.974
" 0.97 "	0.970	....
" 0.97 "	0.968	....
No. 5616	0.677	0.676
No. 5561	0.789	0.798
No. 5566	0.806	0.803
No. 5557	0.780	0.782
No. 4367 (a tungsten steel)	2.060	2.017
Standard 1.15 per cent	1.150	1.155
" 1.15 "	1.150	1.149
" 1.15 "	1.150	1.146
" 1.15 "	1.153	1.153
" 1.15 "	1.145	1.143
" 1.15 "	....	1.146

[1] This Journal, **22**, 210.

It will be noticed that rather high carbon steels only have been dealt with and no irons. It is well known that mild steels and irons are more readily attacked by acid than high carbon steels. I have stated that the amount of free acid should not exceed 4.5 cc. per liter. This is a trifle more than sufficient to prevent any precipitation of basic iron salts, yet this solution, if allowed to stand upon a very mild steel or iron, will react with slight evolution of hydrogen. However if a very mild steel or iron be dissolved in this solution, the results vary from those obtained when the copper salt is the decomposing agent by amounts not exceeding the experimental error.

Sample.	Dissolved in $CuCl_2.2KCl$. Per cent. carbon.	Dissolved in $FeCl_3.2KCl$. Per cent. carbon.
No. 23943	0.383	0.388
No. 23943	0.375	0.383
Cast iron { combined carbon = 0.126 per cent. }	3.034	3.060

This would seem to indicate that the very dilute acid reacted upon the ferrite and not upon the cementite and that the carbon released from the Fe_3C by the $FeCl_3$ was not readily taken up by the hydrogen produced from the acid acting upon the ferrite. That cementite resists the action of acid is well known and is shown by the difficulty experienced in dissolving high carbon steel, also by the action of very dilute acid upon a polished specimen of a low carbon steel.

The action of light upon chlorine water is to produce hydrochloric acid and oxygen. Ferric chloride is also affected by the action of the light; hence it may be well to call attention to the fact that the chlorinated solution increases in acid content, particularly if it stands any length of time in the sunlight.

All the results obtaned in investigating the iron salt as a solvent have not been given, but sufficient to show that it can be used. The advantages derived from using it, especially where many determinations are made daily, will be apparent. The ease with which the point when all the drillings have gone into solution, is ascertained, the ready examination of the filtrate for any carbon that may have escaped the filter, and the economy recommend it.

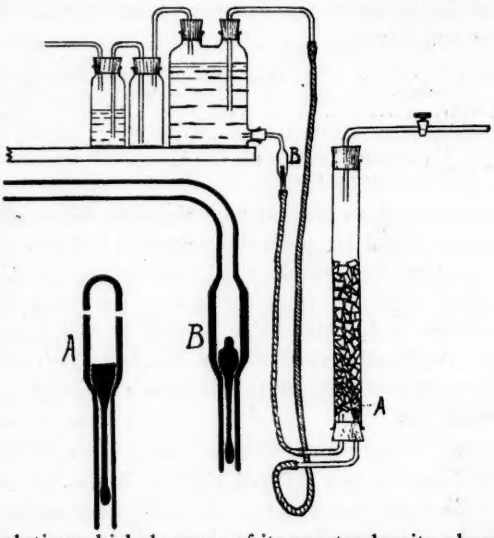
LABORATORY OF THE CARPENTER STEEL CO.,
READING, PA.

AN AUTOMATIC GAS-GENERATOR.

By Henry H. Denham.

Received August 2, 1902.

In the course of some experimental work recently begun the writer was confronted with the want of an automatic gas-generator which would yield at least a moderately steady supply of hydrogen sulphide without the necessity of frequent manipulation. As is well known, the Kipp and other forms of gas-generators in common use have the defect of using over and over the spent acid



and salt solution which, because of its greater density, always settles to the bottom of the apparatus. In order to use the whole of the acid it is consequently necessary to agitate the liquid from time to time. To the writer's knowledge there is but one form of automatic generator on the American market in which this necessity is obviated, and that is somewhat complicated.

With a somewhat limited supply of apparatus at hand, the following arrangement was devised which proved so satisfactory and practicable, and withal so simple of construction, that it seemed worth while to publish a description of it. In this description the dimensions are omitted, as it will readily be seen that the sizes of

the different parts will depend largely upon the gas to be prepared and the quantities in demand. The accompanying sketch will serve to show the general proportions of the apparatus in use in this laboratory.

A two-necked Woulff bottle, tubulated at the bottom, was used as an acid tank. The iron sulphide was contained in a glass tube, closed at its upper end with a one-hole rubber stopper fitted with a glass stop-cock, and at its lower end with a two-hole rubber stopper containing inlet and outlet tubes. The inlet tube terminates in a valve, *A*, opening upward just above the stopper, and is connected by rubber tubing to a glass tube passing through one neck of the acid bottle and terminating somewhat below the shoulder of the bottle. The outlet tube is open, and is connected by rubber tubing with another valve-tube, *B*, opening into the acid bottle through the tubulature at the bottom. The rubber tubes and the Woulff bottle being filled with dilute acid and the latter being placed at a suitable height above the generator, on opening the stop-cock, the acid enters the generator and the flow of gas commences at once. On closing the cock, the back pressure forces the acid from the generator back to the bottom of the acid bottle, and subsequent reopening allows the ingress of fresh acid into the generator. The second neck of the Woulff bottle was in this case connected with a trap for the absorption of any excess of hydrogen sulphide from the spent acid, and consisted merely of two bottles connected by glass tubing and containing a strong solution of potassium hydroxide. This would, of course, be unnecessary in many cases.

Separate sketches show the construction of the two valves, which will offer no difficulties to any one with slight skill in glass tube-working. The valves are simply glass rods of suitable size, drawn out and ground into their seats with turpentine, camphor and emery, before being cut from the long rod. Holes are drilled in the inlet valve-tube *A* by the use of the camphor mixture and a drill made from a round file. To guard against any possibility of the valve in *B* being carried upward by the current of liquid and consequently stopping the upper opening of the valve-tube, its top is pinched flat while still soft in the flame. Devices for washing and drying the gas are omitted from the drawing, as they would obviously vary with the gas and the use to which it was to be put.

BUFFALO CENTRAL HIGH SCHOOL,
July 19, 1902.

THE COPPER ASSAY BY THE IODIDE METHOD.

By Albert H. Low.

Received August 18, 1902.

From time to time the writer has seen statements reflecting on the accuracy of the iodide method for copper. The strictures are undoubtedly, in the main, perfectly just, according to the experience of their authors. When the writer first published his modification of the method, the preliminary experiments and the actual assaying of many ores seemed to justify all the statements then made. Continued use of the method, however, upon all kinds of material, eventually resulted in the discovery of slight inaccuracies under certain conditions not always recognized or understood at the time. Much attention has naturally been paid to the elimination of these troubles and apparently with success. As a result, the assay as now carried out in the writer's laboratory, while essentially the same as originally described, is nevertheless different in many of its details. It appears to leave but little to be desired on the score of accuracy and is perhaps of sufficient general interest to warrant publication.

DESCRIPTION OF THE METHOD.

Standardization of the Thiosulphate Solution.—Prepare a solution of sodium thiosulphate containing about 19 grams of the pure crystals to the liter. Standardize as follows: Weigh accurately about 0.200 gram of pure copper foil and place in a flask of about 250 cc. capacity. Dissolve by warming with 5 cc. of a mixture of equal volumes of strong nitric acid (sp. gr. 1.42) and water and then dilute to about 50 cc. Boil for a few moments to partially expel the red fumes and then add 5 cc. of strong bromine water and boil until the bromine is thoroughly expelled. The bromine is to ensure the complete destructon or removal of the red fumes. Remove from the heat and add a slight excess of strong ammonia water. Ordinarily it suffices to add 7 cc. of ammonia water of 0.90 sp. gr. Again boil until the excess of ammonia is expelled, as shown by a change of color of the liquid and a partial precipitation of the copper as hydroxide or oxide. Now add strong acetic acid in slight excess, perhaps 3 or 4 cc. of the 80 per cent. acid in all, and boil again for a moment if necessary to redissolve the

copper. Cool to room temperature and add about 3 grams of potassium iodide, or 6 cc. of a solution of the salt containing 50 grams in 100 cc. Cuprous iodide will be precipitated and iodine liberated according to the reaction

$$2(Cu.2C_2H_3O_2) + 4KI = Cu_2I_2 + 4(K.C_2H_3O_2) + 2I.$$

The free iodine colors the mixture brown. Titrate at once with the thiosulphate solution until the brown tinge has become weak and then add sufficient starch liquor to produce a marked blue coloration. Continue the titration cautiously until the color due to free iodine has entirely vanished. The blue color changes towards the end to a faint lilac. If at this point the thiosulphate be added drop by drop and a little time be allowed for complete reaction after each addition, there is no difficulty in hitting the end-point within a single drop. 1 cc. of the thiosulphate solution will be found to correspond to about 0.005 gram of copper, or about 1 per cent. in the case of an ore where 0.5 gram has been taken for assay. The reaction between the thiosulphate and the iodine is

$$2(Na_2S_2O_3) + 2I = 2NaI + Na_2S_4O_6.$$

Sodium iodide and tetrathionate are formed. The starch liquor may be made by boiling about 0.5 gram of starch with a little water and diluting with hot water to about 250 cc. The liquor should be homogeneous and free from lumps or grains. It should be used cold and must be prepared frequently, as it does not keep well. The thiosulphate solution made from the pure crystals and distilled water appears to be quite stable, showing little or no variation in a month under reasonable conditions.

Treatment of Ores.—To 0.5 gram of the ore in a flask of 250 cc. capacity add about 6 cc. of strong nitric acid and boil gently nearly to dryness. Then add 5 cc. of strong hydrochloric acid and again heat. As soon as the incrusted matter has dissolved add 6 cc. of strong sulphuric acid (sp. gr. 1.84) and boil until the more volatile acids are expelled and the fumes of sulphuric acid are coming off freely. This is best done over a naked flame. Allow to cool, add 25 cc. of cold water and heat the mixture to boiling. Allow to stand, hot, until any anhydrous ferric sulphate is entirely dissolved and then filter to remove more especially any lead sul-

phate. Receive the filtrate in a beaker about 6 cm. in diameter. Wash the flask and filter with either hot or cold water and make the volume of the filtrate about 75 cc. Place in the beaker a piece of sheet-aluminum prepared as follows: Cut a strip of stout sheet-aluminum 2.5 cm. wide and about 14 cm. long and bend this into a triangle so it will stand upon its edge in the beaker. The same aluminum may be used repeatedly as it is but little attacked each time. Add one large drop of a mixture of equal volumes of strong hydrochloric acid and water, cover the beaker and heat to boiling. Allow to boil from seven to ten minutes, which should be sufficient to precipitate all the copper in any case, provided the bulk of the solution does not much exceed 75 cc. Avoid boiling to a very small bulk, as, in that case, some of the precipitated copper may redissolve. The aluminum should now appear clean, the precipitated copper being detached or only loosely adhering. Remove from the heat and wash down the cover and sides of the beaker with cold water. There is danger of the finely divided copper being slightly oxidized and dissolved during the subsequent washing. To prevent this, and at the same time to precipitate any traces of copper still remaining in solution, add about 15 cc. of strong hydrogen sulphide water. If the copper in the ore does not much exceed 20 per cent. proceed as follows: Decant the supernatant liquid through a 9 cm. filter. Add 10 cc. of strong hydrogen sulphide water to the residue in the beaker and then transfer the liquid and precipitate to the filter. Wash thoroughly with cold water, without delay, to avoid oxidation. Now place the clean original flask under the funnel. Pour over the aluminum in the beaker 5 cc. of a mixture of equal volumes of strong nitric acid (sp. gr. 1.42) and water. Any adhering particles of copper will be thus dissolved. Heat to boiling but do not prolong the latter or the aluminum will be unnecessarily attacked. Pour the hot acid very slowly over the precipitate on the filter so as to dissolve all the copper, lifting the fold if necessary. Now, without washing, pour 5 cc. of a cold, saturated, aqueous solution of bromine into the filter and then wash the beaker and filter with hot water. Finally remove the filter and open it. If there remains a residue that might possibly contain copper it may be rinsed into the flask. The bromine has several functions. It cleanses the separated sulphur left on the

filter, it ensures the highest state of oxidation of any arsenic or antimony present, and it also effects the complete destruction or removal of the red fumes, which is a matter of great importance. If 5 cc. of bromine water are insufficient to impart a permanent tinge to the filtrate, more must be added. Boil the filtrate, which usually does not exceed 75 cc. in bulk, to thoroughly expel the excess of bromine, but avoid boiling to such a small bulk as to cause decomposition of bromides, etc. Remove from the heat and add ammonia water in slight excess (ordinarily 7 cc. of strong ammonia). Boil off the excess of ammonia, as shown by the change of color of the solution, and then acidify with acetic acid, again boiling if necessary to redissolve any precipitate containing copper. The addition of 3 or 4 cc. of the 80 per cent. acid is usually sufficient. A large excess of acetic acid does no harm but is not necessary except in the presence of sufficient arsenic to cause a precipitate of copper arsenate. This may require considerable acetic acid for its solution, perhaps 10 cc. If not mostly dissolved at this stage, it is taken up slowly later on and the titration may become very tedious before the true end-point is finally reached. Proceed with the acetic acid solution, after cooling to room temperature, precisely as described in the standardization of the thiosulphate and calculate the percentage of copper from the amount of the latter required.

In titrating low percentages of copper great care should be taken not to pass the end-point. Always work slowly towards the end and stop short of complete decolorization and then continue only when the liquid, after standing a minute or two, still persists in a tinge of color.

With high percentages it is usually advisable to wash the precipitated copper by decantation instead of on the filter. Proceed as follows: Transfer the liquid and copper in the beaker (to which hydrogen sulphide solution has been added) to the original flask and set the beaker and aluminum aside temporarily. Allow to settle, decant through the filter and wash the copper three or four times by decantation, the first time with hydrogen sulphide water and then with cold water, using about 20 cc. each time. Now place the flask and residue under the funnel, heat the 5 cc. of acid in the beaker as before and pour it through the filter. Do not add

the bromine for the moment but remove the flask, replacing it under the funnel with the beaker, and heat the acid until all the copper is dissolved and the red fumes are mostly expelled. Now return the flask under the funnel, add the bromine, proceed with the washing of the beaker and filter, and continue as described above.

Owing to the fact that the end-pont is somewhat sharper as the amount of copper present is less, the operator may perhaps find it advantageous in the case of very rich material to take only 0.25 gram instead of 0.5 gram for assay. As there seems to be no difficulty in doing accurate work by either plan, this is perhaps best left a matter of choice.

Notes.—According to the equation previously given, 0.5 gram of copper requires 2.62 grams potassium iodide. While direct experiment shows this to be apparently true, yet when only the theoretical amount of potassium iodide is present the reaction is slow and in fact does not appear to proceed to completion until during the titration, which is thereby unduly prolonged. It is best, therefore, to always use an excess, but as the iodide is expensive the quantity used should be governed by the amount of copper present, which can always be estimated approximately. Allow say 1 gram potassium iodide for every 15 per cent. copper, when 0.5 gram of ore is taken for assay. It is convenient to prepare a solution containing 50 grams of potassium iodide in 100 cc. A 2 cc. pipette will thus deliver 1 gram of the salt. No error will be introduced in a doubtful case by adding more potassium iodide after the titration is apparently finished and resuming the operation if the blue color is thereby restored.

Zinc and silver do not interfere with the assay. Lead and bismuth are without effect, except that by forming colored iodides they may mask the approach of the end-point before adding starch. Arsenic and antimony, when fully oxidized as described, have no influence. The return of the blue tinge in the titrated liquid after long standing is of no significance, but a quick return, which an additional drop or two of the thiosulphate does not permanently destroy, is usually an evidence of faulty work.

DENVER, COLORADO, August 14, 1902.

THE QUANTITATIVE DETERMINATION OF SELENIUM IN ORGANIC COMPOUNDS.

By R. E. Lyons and F. L. Shinn.

Received August 20, 1902.

The difficulties encountered in the estimation of selenium in organic compounds led to a study of the analytical methods in use. We have found these methods impracticable in their application to selenium compounds which are to be decomposed with nitric acid. The results obtained were invariably too low.

It is stated in the literature,[1] and has been verified in this laboratory, that when metallic selenium is oxidized by nitric acid, the product is always selenious acid without a trace of selenic acid. This statement holds good in the case of organic compounds containing selenium when they are heated with red nitric acid in a sealed tube for several hours at temperatures between 180° and 260° C. Advantage has been taken of this deportment for the determination of selenium by methods based upon the reducibility of selenious acid by sulphur dioxide, hydrogen sulphide, sodium thiosulphate, hydriodic acid, etc.

The determination of selenium in solutions of selenious acid free from nitric acid is comparatively easy. Several of the methods proposed permit of a high degree of accuracy. The two following have best served our purpose:

(1) The old gravimetric method of Rose,[2] which consists in reducing the selenious acid, in the presence of hydrochloric acid, by means of sulphur dioxide, collecting the precipitate on a weighed paper, drying at 100° C., and weighing.

(2) The iodometric method of Norris and Fay,[3] whereby the selenious acid is reduced, in the presence of hydrochloric acid, by an excess of N/10 sodium thiosulphate solution and the excess determined by titrating back with a standard iodine solution.

Both methods when properly executed yield excellent results. The volumetric process is preferable when a number of estimations are to be made. It is simple, rapid and accurate.

Other methods deserving mention are those of Gooch and

[1] Wohlwill: *Ann. Chem. Pharm.*, **114**, 173; Dammer: Band **1**, 683; Roscoe and Schorlemmer: Vol. **1**, 362.

[2] Pogg. *Ann.*, **113**, 472; *Zischr. anal. Chem.*, **1**, 73.

[3] *Am. Chem. J.*, **18**, 703; **23**, 119.

Pierce,[1] and Muthman and Schaeffer.[2] The latter method, however, has been studied by Gooch and Reynolds[3] and found to be inaccurate.

None of these methods are directly applicable to solutions of selenious acid containing free nitric acid, a condition obtaining from the customary oxidation of selenium and its compounds with nitric acid. To free such solutions from nitric acid without loss of selenium has afforded great difficulty from the time of the first attempts to estimate this metal.

Rose[4] states that solutions of selenious acid can not be heated above 100° C. without volatilization of selenium dioxide and provides for the removal of the nitric acid by evaporation on a water-bath. It has been our experience, and the experience of others, that with the most carefully conducted evaporations a loss of selenium invariably occurs.

Divers and Schimose[5] attribute the low results to the formation of selenic acid during the evaporation with nitric acid. They recommend boiling the residue with hydrochloric acid for the purpose of reducing any selenic acid to selenious acid. This precaution is manifestly unnecessary when nitric acid alone has been used to decompose the compound.

Rathke[6] recommended the addition of hydrochloric acid to the selenious acid solution previous to evaporation. Later,[7] he suggested the addition of sodium or potassium chloride to the solution to prevent volatilization of selenium chloride during the repeated evaporations with hydrochloric acid. The results of Rathke's analyses show a loss of from 1 to 5 per cent.

Michaelis,[8] finding that evaporation with hydrochloric acid always resulted in the loss of selenium, sought to avoid evaporation by boiling the solution with a great excess of concentrated hydrochloric acid until the nitric acid should be completely decomposed. The operation was conducted in a flask provided with a return condenser. Michaelis used this scheme success-

[1] *Am. J. Sci.*, **1**, (4), 31.
[2] *Ber. d. chem. Ges.*, **26**, 1008.
[3] *Am. J. Sci.*, **50**, 254.
[4] *Ztschr. anal. Chem.*, **1**, 73.
[5] *J. Chem. Soc.*, **57**, 439.
[6] *Ann. Chem. Pharm.*, **152**, 194 and 206.
[7] *J. prakt. Chem.*, **108**, 249.
[8] *Ber. d. chem. Ges.*, **30**, 2827.

fully, in connection with the gravimetric method, when ordinary nitric acid was employed to bring about the decomposition of the organic compound. It is our experience that when as little as 4 or 5 cc. of red fuming nitric acid are used, several hours' boiling under an inverted cooler is not sufficient to bring about complete decomposition and removal of the nitric acid. The method, even should it be successful, is a very great time-consumer and is troublesome from a mechanical standpoint. Further, the solution of selenious acid so treated would be unfit for direct titration, according to the method of Norris and Fay, on account of the large and unknown amount of hydrochloric acid present. It has been demonstrated that for accurate results with the method of Norris and Fay the amount of hydrochloric acid employed must fall within a certain, well-defined limit.[1]

The method suggested in this paper for the elimination of the nitric acid has the advantage of easy execution, requires less time and attention, and gives very accurate results when used in connection with either the gravimetric or volumetric methods for determining the selenium in solutions of selenious acid.

In the attempted estimations of selenium in a number of compounds, some of which contained mercury, we observed that in the case of a mercuric chloride compound the results always came nearer the theoretical than was true with the purely organic compounds. This deportment is verified in the analytical results reported by Rathke.[2] In a body, $C_3H_5Se_2OK$, the selenium found was 58.21 per cent. (theory 62.36 per cent.), while in the compound $2Se(C_2H_5)_3Cl + ZnCl_2$, containing the heavy metal zinc, the selenium found was 28.59 per cent. (theory 29.44 per cent.).

The plausible explanation of this deportment is that the heavy metal present forms with the selenious acid a selenite which is stable at the temperature of the water-bath, thus retaining all of the selenious acid in combination during the evaporation.

Accordingly, exactly equivalent portions of mercuric nitrate were weighed out and dissolved in the selenious acid solution previous to evaporation. The results were encouraging rather than satisfactory. The quantity of selenium usually lost by

[1] Norton: *Am. J. Sci.*, **157**, 287: Norris and Fay: *Am. Chem. J.*, **23**, 123.

[2] *Ann. Chem. Pharm.*, **152**, 207-212.

evaporation in the absence of a heavy metal was found much diminished. It would be impracticable, for obvious reasons, to have in the solution always a quantity of mercury salt exactly equivalent to the selenious acid. It became evident that the metal added to the solution to retain the selenious acid during the evaporation must form a selenite perfectly stable at 100° C., and sufficiently insoluble in cold water to permit of washing free from nitrates and nitric acid. A number of simple selenites, *e. g.*, cadmium, mercury, magnesium and silver, were tried but without success. All were found too soluble for quantitative purposes. A further search in the literature was rewarded by finding the statement of Boutzoureano[1] concerning the double selenite ammonia compounds. A number of selenites dissolve in ammonium hydroxide and upon evaporation of the solution on a water-bath, or in a vacuum, form double compounds, *e. g.*, $Ag_2SeO_3NH_3$. Silver and zinc selenite ammonia may be formed in this way. These compounds are insoluble in water, soluble in acids and perfectly stable at 100° C.

It was foreseen from this, that if to a solution of selenious acid containing nitric acid an excess of silver or zinc nitrate be added and the solution evaporated to dryness to expel the nitric acid, the residue, containing all of the selenium as selenite, could then be evaporated with ammonium hydroxide to form the double selenite ammonia. This compound, it was hoped, would permit of washing free from nitrates without appreciable loss. The residue of silver or zinc selenite ammonia could then be decomposed by means of hydrochloric acid, and the usual gravimetric or volumetric methods for the estimation of selenious acid applied. The method was tried and proved entirely successful.

EXPERIMENTAL PART.

Preparation of Pure Selenium Dioxide.—Pulverized selenium was oxidized with concentrated nitric acid and the reaction mixture evaporated to dryness on a water-bath. The residue was moistened with nitric acid and sublimed in a small beaker according to the method suggested by Norris and Fay.[2] To ensure greater purity the above product was resublimed in a current of

[1] *Jahresb. u. Fortschritte d. Chem.*, **42**, 398.
[2] *Am. Chem. J.*, **18**, 704.

dry oxygen in a combustion tube. The selenium dioxide so obtained, in the form of delicate, white needles, was dried to constant weight in a vacuum desiccator over phosphorus pentoxide. An accurately weighed quantity of pure selenium dioxide was dissolved in water, the solution acidulated with a drop of concentrated hydrochloric acid and diluted to 1000 cc.

In all of the following experiments the volumetric method of Norris and Fay[1] was used for the final estimation of the selenious acid.

Direct Titration of the Selenious Acid Solution.—Portions of the selenious acid solution, 25 cc. each, were titrated directly with the following result:

	Selenium present. Gram.	N/10 $Na_2S_2O_3$ used. cc.	Selenium found. Gram.
(*a*)	0.05468	27.69	0.05469
(*b*)	0.05468	27.63	0.05457
(*c*)	0.05468	27.65	0.05461

Determination of Selenium in Solutions Containing Nitric Acid.—(*a*) Portions of 25 cc. of the selenious acid solution were treated with a slight excess of silver nitrate and about 2 cc. of fuming nitric acid. The evaporation to dryness and repeated treatment with ammonium hydroxide was then carried out according to the method to be described later. Following are the results:

	Selenium present. Gram.	N/10 $Na_2S_2O_3$ used. cc.	Selenium found. Gram.
(*a*)	0.05468	27.83	0.05498
(*b*)	0.06491	32.78	0.06472
(*c*)	0.06491	32.88	0.06489
(*d*)	0.06491	32.75	0.06468
(*e*)	0.06491	32.77	0.06470

(*b*) An excess of zinc nitrate was used instead of silver nitrate in a series of experiments similar to (*a*), with the following result:

	Selenium present. Gram.	N/10 $Na_2S_2O_3$ used. cc.	Selenium found. Gram.
(*a*)	0.06491	32.71	0.06460
(*b*)	0.06491	32.75	0.06468

(*c*) Similar experiments were made using cadmium nitrate in place of silver or zinc nitrate. The results were very much too low. Cadmium selenite ammonia, $CdSeO_3.NH_3$, does not withstand the washing.

[1] *Am. Chem. J.*, **18**, 704; **23**, 119.

(*d*) The selenium in the following aromatic selenium compounds was determined by this process:

	Weight of substance.[1]	Evaporated with zinc or silver nitrate.	N/10 $Na_2S_2O_3$ used. cc.	Se present.	Se found.	Theory. Per cent.	Found. Per cent.
(1)	0.10745	$AgNO_3$	27.52	0.05444	0.05436	50.67	50.59
(2)	0.21445	$Zn(NO_3)_2$	54.78	0.10866	0.10819	50.67	50.46
(3)	0.09065	$AgNO_3$	21.23	0.04212	0.04193	46.47	46.25
(4)	0.0945	$AgNO_3$	14.84	0.02950	0.02931	31.22	31.01

We recommend the following procedure for the determination of selenium in organic compounds:

Heat a weighed quantity of the substance in a sealed tube with red fuming nitric acid one hour, or longer, at a temperature of 235° or 240° C. Transfer the contents of the tube, together with the wash-water, to an evaporating dish of about 400 cc. capacity. Add about 1/4 more silver or zinc nitrate than is theoretically required to unite with the selenious acid present. Evaporate to dryness on a water-bath.[2] Wash down the sides of the dish with a little water and again evaporate to dryness. Treat the residue twice with about 50 cc. dilute ammonium hydroxide and evaporate after each addition. Add water and evaporate twice to ensure complete removal of free ammonia. When cool, wash the residue with water, decanting the wash-water on a filter, until free from nitrates. Place the filter-paper in the evaporating dish, decompose the silver or zinc selenite ammonia with 10 cc. hydrochloric acid (sp. gr. 1.124), dilute the solution to about 300 cc. with water and add a few pieces of ice.

Run in N/10 sodium thiosulphate solution in slight excess,[3] allow the mixture to stand one hour[4] and determine the excess of thiosulphate by titration with standard iodine solution.

1 cc. N/10 $Na_2S_2O_3$ solution = 0.001975 gram of metallic selenium.

To estimate the selenium gravimetrically:

(*a*) In case silver nitrate is used: Filter after decomposing the

[1] The substance used in (1) and (2) is di-phenyl-di-selenide; in (3) di-benzyl-di-selenide; and in (4) a compound, $C_{27}H_{24}Se_2$.

[2] The water-bath must not be allowed to go dry during this or any subsequent evaporation.

[3] We have found this method most accurate when the excess of N/10 thiosulphate employed does not exceed 5 to 7 cc. Compare Norton: *Am. J. Sci.*, **157**, 287; also Norris and Fay: *Am. Chem. J.*, **23**, 123.

[4] The mixture must be kept near the temperature of melting ice during the reduction with thiosulphate.

silver selenite ammonia with hydrochloric acid, wash the paper free from chlorine and reduce the selenious acid in the filtrate by means of sodium bisulphite.

(*b*) In case zinc nitrate is used: Filtering after the decomposition with hydrochloric acid may be omitted.

INDIANA UNIVERSITY, BLOOMINGTON, IND.,
August, 1902.

[CONTRIBUTION FROM THE LABORATORY OF THE PENNSYLVANIA STATE COLLEGE EXPERIMENT STATION.]

THE DETERMINATION OF SULPHUR AND PHOSPHORUS IN PLANT SUBSTANCES.

BY C. P. BEISTLE.

Received September 3, 1902.

IT IS commonly known to chemists that plant materials, in their conversion to ash by burning, lose not only water, carbon dioxide, and nitrogen as the gaseous products of their ignition, but generally some portion of their sulphur and phosphorus as well.[1] Experience of other analysts has shown that such losses can not be avoided, like those of alkaline chlorides, by any simple precaution. The accurate determination of sulphur and phosphorus is of great importance in calculating the heat of combustion in plant substances from their elementary analysis, and the determination of phosphorus in estimating the soil-exhausting action of vegetable products. The ordinary ash analysis is insufficient for such purposes.

The following work was undertaken at the suggestion and under the direction of Dr. William Frear. The determination of sulphur and phosphorus in plant substances is carried on by a number of different methods and a comparison of results on a few of these methods is all that was attempted. The substances analyzed were cottonseed-meal and timothy hay. There were also a few determinations made on egg albumen. These substances were chosen on account of the wide difference in their sulphur and phosphorus content, the cottonseed-meal containing relatively large amounts, while the timothy hay is very poor in these elements. The methods used were as follows:

[1] Wiley's "Principles and Practice of Agricultural Analysis," Vol. I, pp. 419-420; Vol. III, pp. 37, 430 and 446.

First. Determination of the sulphur and phosphoric acid in the ashes of the substances.—About 5 or 10 grams of the sample were incinerated in a platinum dish; the ash was digested with a little dilute hydrochloric acid and then washed on a filter with hot water. The filtrate and washings were made up to about 150 cc. and then, while hot, barium chloride solution was added. After standing twelve hours, the solution was filtered, and the barium sulphate was washed, ignited, and weighed; the amount of sulphur was calculated from the weight of barium sulphate. The filtrate and washings from the barium sulphate precipitation were evaporated to a small bulk, the hydrochloric acid neutralized with ammonia and the solution was acidified with nitric acid. Phosphoric acid was then determined in the usual way with ammonium molybdate and magnesia mixture.

Second. Destruction of organic matter by fusion with potassium hydroxide and nitrate and determination of sulphur and phosphoric acid in the fused mass.—Two grams of the sample were fused with a mixture of 20 grams of potassium hydroxide and 6 or 8 grams of potassium nitrate. The fusion was made in platinum crucibles heated by gasoline gas. Blank determinations were made, which gave no trace of sulphur or phosphorus, showing both the purity of the reagents used, and that no sulphur was absorbed from the gas. After complete fusion was obtained the mass was cooled, dissolved in hot water, and then carefully acidified with hydrochloric acid. Sulphur and phosphoric acid were determined in this solution as before. A blank determination was made on the potassium hydroxide and potassium nitrate but neither sulphur nor phosphoric acid was found.

Third. Destruction of organic matter by action of potassium hydroxide followed by chlorine, and determination of sulphur and phosphoric acid in residues.—Two grams of the sample were boiled with about 200 cc. of a strong potassium hydroxide solution for thirty minutes. Chlorine was then passed through the solution till it was decolorized. The solution was then acidified with hydrochloric acid and filtered. The sulphur and phosphoric acid in the solution were determined in the usual way.

Fourth. Destruction of organic matter by ignition with oxygen in a bomb-calorimeter and determination of the sulphur and phos-

phoric acid in the products of combustion.—A 2-gram sample was pressed into a small tablet and placed in a Hempel-Atwater bomb-calorimeter. The bomb was then filled with oxygen at a pressure of 18 atmospheres. The sample was ignited by an electric fuse. During combustion, the bomb was surrounded by cold water, as is usual in determining heats of combustion, and kept thus cooled for fifteen minutes, so that the condensation of the vapors formed in the bomb might be as complete as possible. Owing to the high pressure of the gases enclosed within the bomb and the nature of its vent, the regulation of their escape, in such manner as to ensure the complete absorption of any substances containing sulphur or phosphorus that might have escaped condensation, seemed impossible. The method is, therefore, valid only in so far as the sulphur and phosphoric acid are retained in the solid and liquid residues within the bomb. The liquid contained only traces of phosphoric acid, this constituent appearing chiefly in the solid residues. After the ignition, the bomb was opened, the liquid it contained was washed into a beaker and the small amount of ash, which was usually in the form of an insoluble glassy slag, was fused with sodium carbonate. This fusion was dissolved in hot water, and the solution added to the liquid washed from the inside of the bomb. The sulphur and phosphoric acid were then determined in the solution.

Fifth. Destruction of organic matter by a boiling mixture of nitric and hydrochloric acids, and determination of sulphur and phosphoric acid in the resulting solution.—The samples were treated according to the method of the Association of Official Agricultural Chemists for total phosphoric acid. Two grams of the sample were boiled for thirty minutes in a mixture of nitric and hydrochloric acids. The sulphur and phosphoric acid were determined in the solution. In some of the determinations on cottonseed-meal the boiling was carried on for a much longer time and the acid lost by evaporation was replaced by more acid.

Sixth. Destruction of organic matter by burning in oxygen in a combustion tube and determination of sulphur and phosphoric acid both in the residual and escaping gases.—The sample was burned in a combustion tube in a current of oxygen. The products of combustion were passed through a series of absorption tubes

containing a hydrochloric acid solution of bromine. After the combustion was completed, the solution in the absorption tubes was emptied into a beaker. The combustion tube was washed out to remove the ash, and the washings were added to the solution from absorption tubes. The mixed solutions were boiled till all the bromine was expelled, and then filtered. The sulphuric acid was then determined in the clear solution as usual. The complete combustion of the organic matter was attained with difficulty; undecomposed vapors tended to form a tarry deposit at the exit end of the tube; this was finally overcome, first, by introducing the oxygen not only at the end of the combustion tube, but also, by means of a small tube inserted at a point about an inch beyond the boat containing the burning material; and, second, by taking pains to keep the tube at a bright red heat for a few inches beyond the entrance of the second stream of oxygen. With these precautions, no condensaton of tarry products occurred. To secure the most complete contact of the escaping gases with the bromine solution, the latter was held in four 6-inch, 3-bulb U-tubes set in a pan of cool water, and the gases were evolved slowly as in a carbon determination.

Seventh. Ignition after saturation with a solution of calcium acetate.—The sulphur was also determined according to a modification of the method proposed by A. E. Shuttleworth of Ontario Agricultural College. Ten grams of the sample were saturated with 20 cc. of a solution of calcium acetate containing 29.2 grams to the liter. The material was then incinerated and sulphur determined in the ash. These incinerations took place in a platinum crucible.

Eighth. Ignition after saturation with a solution of barium hydroxide.—Ten grams of the cottonseed-meal were saturated with a solution of barium hydroxide, dried, and ignited. The ash was fused with sodium carbonate, the fused mass extracted with hot water, the solution filtered and the sulphur determined in the filtrate as usual.

A partial analysis of the organic substances used, was made with the following results:

TABLE I.—FODDER ANALYSIS OF MATERIALS.

	Moisture.		Fat.		Protein.[1]	Ash.	
Cottonseed-meal ..	7.08	7.13	10.05	10.00	42.12	5.73	5.70
Timothy hay	4.55	4.50	2.02	2.02	4.75	3.81	3.84
Egg white (dry)..	...	...	...	...	83.37	6.02	...

As previous statements indicate, the results are somewhat differently expressed for the two elements under consideration, those for sulphur being given in terms of the element itself, those for phosphorus in terms of the pentoxide, P_2O_5, commonly spoken of, in agricultural chemical literature, as "phosphoric acid". The reason for the distinction is that evidence points to the existence of phosphorus in plants principally in the form of phosphoric acid, except in the seeds where it exists largely in the organic form in lecithins and other similar compounds; and to the fact that sulphur is present principally in some other state of combination than sulphuric acid.

The following experiment clearly shows this fact. Any sulphates present in a plant substance can be removed by careful extraction with hydrochloric acid of moderate strength and can be precipitated from the solution directly. The cottonseed-meal was thus extracted with acid of 1.06 sp. gr.; the solution contained sulphuric acid (SO_3) equivalent to 0.159 per cent. of the meal (as the result of duplicate, exactly concordant determinations); this corresponds to 0.064 per cent. of sulphur, about one-ninth of all the sulphur present.

The results of the several determinations of sulphur and phosphoric acid in cottonseed-meal and timothy hay by the foregoing eight methods are presented in Tables II-IV.

TABLE II.—SULPHUR.

	Cottonseed-meal.			Timothy hay.	
Methods.	I. Per cent.	II. Per cent.		I. Per cent.	II. Per cent.
1. In ash	0.046	0.040	....	0.048	0.042
2. Fusion with potassium hydroxide and nitrate	0.570	0.550	....	0.145	0.135
3. Destruction by potassium hydroxide and chlorine	0.280	0.280	....	....	....
4. In bomb-calorimeter products..	0.440	0.410	....	0.075	0.068
5. In solution with hydrochloric and nitric acids	0.230 / 0.220[2]	0.240 / 0.230[2]	.....	....	....

[1] Nitrogen × 6.25.

[2] After extraction with ether.

Methods.	Cottonseed-meal. I. Per cent.	Cottonseed-meal. II. Per cent.		Timothy hay. I. Per cent.	Timothy hay. II. Per cent.
6. In products of ignition in combustion tube	0.470	0.440	0.450	....	....
7. Ignition after saturation with calcium acetate	0.120	0.120	....	0.044	0.044
8. Ignition after saturation with barium hydroxide	0.065	0.070	....	....	....

TABLE III.—PHOSPHORIC ACID.

Methods.	Cottonseed-meal. I. Per cent.	Cottonseed-meal. II. Per cent.	Timothy hay. I. Per cent.	Timothy hay. II. Per cent.	Timothy hay. III. Per cent.
1. In ash	2.41	2.31	0.355	0.345	...
2. Fusion with potassium hydroxide and nitrate	2.51	2.45	0.34	0.32	...
3. Destruction by potassium hydroxide and chlorine	0.42	0.46	...	...	...
4. In bomb-calorimeter products	2.21	2.34	0.29	0.29	...
5. In solution with hydrochloric and nitric acids	1.33	1.33	0.35	0.36	0.32
6. In products of ignition in combustion tube	0.78[1]	0.73[1]	...	...	...

[1] After extraction with ether.

TABLE IV.—ANALYSIS OF EGG ALBUMEN.

Method.	Calculated to dry substance. Sulphur.	Phosphoric acid.
1. In ash	0.196	0.21
2. Fusion with potassium hydroxide and nitrate	1.60	0.22

Sulphur.—It will be seen from these results that the fusion with potassium hydroxide and potassium nitrate gave the highest results for sulphur in all three of the substances examined, and that this method gave results on sulphur in egg albumen closely coinciding with those found by Hoppe-Seyler in the same substance; *viz.*, 1.57 per cent. The amount of sulphur in the ash of the various samples is so low that it gives no indication of the total amount of sulphur present, showing that the greater portion is driven off by ignition. The sulphur obtained by boiling with potassium hydroxide solution, with subsequent oxidation with chlorine, gave only half the sulphur found by the fusion method. The sulphur found by ignition in the bomb-calorimeter is about the same in amount as that found by combustion in a stream of oxygen and absorption of the products of combustion in a hydrochloric acid solution of bromine, but is still considerably less than

is obtained by fusion.[1] It seemed to be impossible to completely oxidize and fix all the sulphur by any other method than by fusion with alkaline nitrate. The methods of saturating the substance with barium hydroxide solution and calcium acetate solution, respectively, before ignition, give results considerably higher than simple incineration without previous saturation; still, they are so far below those given by other methods that they are of slight value.

The great difficulty in the determination of sulphur in organic substances is to get all the sulphur completely oxidized. This was shown by the fact that when cottonseed-meal was fused with potassium hydroxide without enough nitrate being added to completely burn up the organic matter, the results were too low; also, the fusion thus obtained gave off hydrogen sulphide gas when treated with hydrochloric acid, showing that part of the sulphur had been fixed by the alkali but not oxidized.

Phosphoric Acid.—The fusion method gave slightly more phosphoric acid than the ash in the case of the cottonseed-meal, but practically the same for the timothy hay and egg albumen. This would indicate that in the substances examined, the phosphoric acid was volatile to a very slight extent if it all. Boiling with potassium hydroxide solution and treating with chlorine gave results so low, that this method may be discarded for the analysis of this class of bodies. The phosphoric acid found by ignition in the bomb-calorimeter was slightly less than by fusion, and this difference was probably due to mechanical loss of the smaller particles of the glassy slag which contained almost all the phosphoric acid.

The amount of phosphoric acid obtained from the hay by boiling with nitrohydrochloric acid was practically the same as found by fusion or incineration. When the cottonseed-meal was treated in this way only about half of the phosphoric acid present was obtained. It was thought at first that the phosphoric acid had not been taken into solution. When a sample of the cottonseed-meal was placed on a paper filter and extracted with nitric acid (sp. gr. 1.15), the phosphoric acid determined in the filtrate by direct precipitation amounted to 0.16 per cent. Other samples were treated as above, except that the filtrate was evaporated to dryness, the residue ignited, cooled, and then dissolved in nitrohydrochloric

[1] [See, however, the following article. EDITOR.]

acid. The phosphoric acid was determined in the resultant solution, and in three determinations the results were respectively 2.18, 2.22, and 2.31 per cent. This shows that the phosphoric acid was readily taken into solution by the action of nitrohydrochloric acid on the seed meal, but in such form that it could not be entirely precipitated by ammonium molybdate till after ignition and subsequent solution in nitric acid. Work done by Hardin[1] indicates the presence of meta- and pyrophosphoric acid in cottonseed-meal; but these forms of phosphoric acid should be converted into orthophosphoric acid by boiling with strong nitric acid.

Possibly the phosphoric acid in cottonseed-meal is in organic combination that is not broken up by boiling with strong nitrohydrochloric acid and can only be set free by ignition or fusion.

The cottonseed-meal was extracted with anhydrous ether, and the ether extract was fused with potassium hydrodixe and potassium nitrate and the sulphur and phosphorus determined. The extract contained 0.47 per cent. phosphorus pentoxide, probably contained in ether-soluble lecithins; most of the phosphorus in these compounds is driven off by ignition and this would account for some of the difference in results between the methods of fusion with alkali and simple ignition.

The sulphur obtained from the ether extract by the fusion method amounted to 0.30 per cent. of the extract, or calculated to original substance, 0.03 per cent.

[Contribution from the Havemeyer Laboratories of Columbia University, No. 71.]

THE DETERMINATION OF SULPHUR AND PHOSPHORUS IN ORGANIC MATERIALS.

By H. C. Sherman.

Received September 17, 1902.

THE DETERMINATION OF SULPHUR.

In order to secure complete oxidation of the sulphur of organic materials without loss through the formation of volatile compounds a great many modes of procedure have been described. Without attempting an enumeration of these it may be said that nearly all of them fall under one of three general heads:

[1] Bulletin 35 U. S. Dept. of Agriculture, Division of Chemistry, p. 50.

(1) oxidation by means of nitric acid in a sealed tube; (2) heating in a combustion tube in a current of air, oxygen or some oxidizing vapor—the oxidation being sometimes completed by means of platinized asbestos; (3) fusion with an alkali (sometimes with previous treatment with nitric acid), the oxidation being completed either by the addition of an oxidizing agent to the fusion or by treating the alkaline solution with chlorine or bromine. The first method is quite inconvenient for samples low in sulphur because only small amounts of material can be decomposed at a time and determinations are frequently lost through breaking of the tubes. The second method requires the fitting up of special apparatus and is not apt to be used unless many determinations are required. Hence some modification of the third general method is apt to be preferred and the most common is perhaps the fusion of the substance with sodium hydroxide with the addition of nitrate or peroxide to complete the oxidation. This method, if carefully carried out, can be made to yield very accurate results, at least with ordinary materials, but it appears that equally accurate results can be more conveniently obtained by direct combustion in oxygen.

Berthelot in 1892[1] proposed the use of the calorimetric bomb for the elementary analysis of organic substances and stated that on combustion with 25 atmospheres of oxygen the sulphur, as well as the carbon and hydrogen, was completely oxidized, and in the presence of moisture remained entirely in the form of sulphuric acid. This method has been used to some extent, especially for the determination of sulphur in coals, and Hempel has described[2] a modification in which the combustion is accomplished in a large glass vessel with oxygen at ordinary pressure.

As an additional precaution the gases from the bomb after the combustion may be made to pass through bromine water to which the rinsings of the combustion chamber may afterwards be added and the whole boiled to insure the oxidation of any sulphurous acid which may have been formed. This is considered unnecessary by Hempel and the following experiments show that the bromine was not needed with the samples here used: Dried meat, dried curd and white of egg were burned and the sulphur deter-

[1] *Compt. rend.*, **114**, 317, 318.
[2] *Ztschr. angew. Chem.* (1892), pp. 393-394.

mined as described below with the additional precaution of the use of bromine as just mentioned. The same samples were then treated in exactly the same way except that the wash-bottle through which the escaping gases passed contained only water, which was subsequently used for rinsing out the combustion chamber. After passing through the water the escaping gases were led through a second wash-bottle containing bromine water. The same portion of bromine water was used for these three combustions and was then examined and found to have absorbed no sulphur. The results with and without the use of bromine were as follows:

	Percentage of sulphur found.	
	Using bromine water.	Using water only.
Dried lean meat	0.814	0.816
Dried curd	0.611	0.609
Dried white of egg	1.406	1.410

These tests seemed to show conclusively that for these samples the use of bromine was entirely unnecessary and in the subsequent use of this method we have carried it out as follows:

Compressed Oxygen Method.—A suitable amount of sample is pressed into a pellet and burned in the bomb-calorimeter[1] in the same manner as in the determination of heat of combustion, using from 25 to 30 atmospheres of oxygen. By means of a coupling with small bore the bomb is then connected with a wash-bottle containing water, and the gas is allowed to bubble through the water until the contents of the bomb reaches atmospheric pressure, when it is opened and thoroughly rinsed with water. In order to keep down the volume, the water from the wash-bottle is used for the first rinsing. Any ash found in the combustion capsule is dissolved by means of hydrochloric acid and this solution added to the main solution. The whole is then boiled down to the desired volume, filtered if necessary, and the sulphuric acid determined by precipitation with barium chloride.

This method has been applied to a few sulphur compounds prepared by students in the organic laboratory, selecting such as contained sulphur in an "unoxidized" condition in order to make the test as decisive as possible. The following results were obtained:

[1] In these experiments a platinum-lined Atwater-Blakeslee bomb was used.

	Percentage of sulphur.	
	Theoretical.	Found.
Benzyl sulphocyanide	21.49	21.52
Benzyl sulphide	14.96	14.77
Diphenyl thiourea	14.04	13.85
Benzyl sulphoxide	13.92	13.72

The oxygen method was then compared with the alkali method, using sodium peroxide as the oxidizing agent and with the "nitric acid method" as provisionally adopted for the determination of sulphur in plants at the last (1901) meeting of the Association of Official Agricultural Chemists.

Alkali Method.—This was carried out essentially as described by Osborne.[1] Fifteen grams of sodium peroxide were weighed and most of it introduced at once into a large silver crucible and converted into hydroxide by adding a little water and boiling over an alcohol lamp until the excess of water was expelled. The hydroxide was allowed to cool until pasty when the sample was added and stirred into the alkali as quickly as possible. The heat was then gradually raised and the remainder of the peroxide added in small portions to complete the oxidation. The fused mass was then allowed to cool, was dissolved and washed into a beaker with water,[2] acidulated with hydrochloric acid and boiled. Finally the solution was filtered, neutralized with ammonia, brought to the desired volume and acidity and the sulphuric acid determined as usual.

With the vegetable materials the acidulated solution was evaporated to dryness and heated to dehydrate any silica which might have been present.

Nitric Acid Method.—Except that only 2 grams of the sample were taken, the method was carried out as described by Fraps.[3] The material was placed in a 4-inch porcelain evaporating dish, 20 cc. of concentrated nitric acid added and the mixture heated on the water-bath, cautiously at first and then at the temperature of boiling-water. When frothing had ceased and the solution was partly evaporated, 10 cc. of a 5 per cent. solution of potassium nitrate were added and the mixture evaporated to dryness and ignited, at first very cautiously over a Bunsen burner and finally

[1] This Journal, **24**, 142.

[2] In one case it was necessary to filter at this point as the crucible had been attacked by the peroxide.

[3] This Journal, **24**, 347.

over the blast-lamp until the residue was white. The residue was dissolved in hydrochloric acid, evaporated to dryness and heated for some time at 110° to 120° to render silica insoluble. Finally the residue was taken up with water and a little hydrochloric acid, filtered, the filtrate brought to the desired bulk and acidity and the sulphuric acid determined as usual.

With each method about 2 grams of the sample were used in each case and the final precipitation of barium sulphate was made in a solution of about 150 cc. containing about 2 cc. of concentrated hydrochloric acid. The amount of sulphur introduced by the reagents was determined for each method by making a "blank" test with sugar or benzoic acid.

Six samples were used in comparing the three methods. These were: (1) dried lean beef; (2) curd precipitated from cows' milk by acetic acid and reduced to a fine, dry, neutral powder; (3) coagulated yolk of egg, dried, ground and partially extracted with ether; (4) coagulated white of egg, dried and ground; (5) wheat bran; (6) dried beans, outer coating and germ removed before grinding. All of these samples were analyzed in the air-dried state. The results obtained are shown in the following table:

	Percentage of sulphur found.		
Substance.	Compressed oxygen method.	Hydroxide-peroxide method.	Nitric acid method.
Dried lean beef	0.815	0.811	0.679
Dried curd	0.610	0.608	0.495
Yolk of egg	0.822	0.819	0.810
White of egg	1.408	1.421	1.146
Wheat bran	0.264	0.259	0.182
Beans	0.217	0.229	0.165
Average	0.689	0.691	0.580

While the results by the first two methods are practically identical, those obtained by the nitric acid method are lower, the average amount of sulphur found being about five-sixths of that present. A part of this discrepancy is probably due to mechanical loss. Carrying out the method as described it was found in most cases that on heating the residue left on evaporation after the addition of the nitrate, no matter how slowly the heat was applied, there was a short period of vigorous oxidation at about the time the

material had become thoroughly charred. At this point there may easily have occurred a very slight mechanical loss of substance. It seems probable, however, that the greater part of the discrepancy was due to volatilization of sulphur in some form of combination not sufficiently oxidized to stand the heat generated at this point. Such a loss could doubtless be avoided by repeated evaporation with nitric acid or by the addition of alkali along with the nitrate but the method would then become practically that of Salkowski. It is possible also that by sufficient experimentation one might find the proportions of substance, acid, and nitrate which would give good results with a single evaporation, but the proportions would probably differ according to the material to be analyzed and in the writer's hands the method did not promise sufficient advantage to justify such a study. If all loss of sulphur could be avoided, it would become necessary to guard against an absorption of sulphur from the gas flame when the residue is heated over the blast-lamp.

While the results obtained by the first two methods are equally accurate, the combustion in oxygen has some distinct advantages. It requires much less attention, complete oxidation being instantaneously obtained with no danger of loss by volatilization. No reagents are used except the compressed oxygen and a little hydrochloric acid, both of which are apt to be free from sulphur, whereas it is difficult to obtain an alkali which does not contain an appreciable amount. Moreover, by doing away with the use of alkali any danger of absorption of sulphur compounds from the air of the laboratory is avoided and the solution in which the final precipitate is obtained is free from any large amount of foreign salts.

THE DETERMINATION OF PHOSPHORUS.

The following three methods for determination of phosphorus were compared.

Compressed Oxygen Method.—The combustion was carried out as described above. The ash in the platinum combustion capsule was dissolved by means of strong nitric acid and this solution added to the rinsings of the bomb and the whole boiled and then allowed to cool. Ammonia was then added in excess and the solution slightly acidulated with nitric acid and precipitated with molybdate

solution, the ammonium phosphomolybdate being afterward dissolved and the phosphoric acid precipitated with magnesia mixture in the usual manner. The details of manipulation recommended by the Association of Official Agricultural Chemists[1] were here followed, especial care being given to the conditions of the final precipitation.

Sodium Carbonate Method.—The sample was mixed in a platinum dish with 6 or 7 grams of dry sodium carbonate and 3 or 4 grams of the latter spread over the mixture. The dish was then heated carefully over a Bunsen burner until all danger of vigorous reaction was past. The heat was then raised and pulverized potassium nitrate added in small portions, the mass being occasionally stirred with a platinum rod. This was continued until the mass was entirely white, the whole amount of nitrate added being usually about 1 gram. After cooling, the fusion was transferred to a beaker, dissolved in water and nitric acid, and the determination completed as described above.

Sulphuric Acid and Ammonium Nitrate Method.—This was carried out essentially as described by Neumann.[2] The sample is placed in a Kjedahl digestion flask, 20 cc. of concentrated sulphuric acid and 10 grams of ammonium nitrate added, and the mixture heated carefully until frothing ceases, then allowed to cool somewhat and 10 grams more of ammonium nitrate added and the digestion continued until organic matter is entirely destroyed and a colorless solution obtained. This is allowed to cool, washed out into a beaker, about 15 grams of ammonium nitrate added, and the phosphoric acid determined by the molybdate-magnesia method as already described. This method had already been found to yield the same results as the carbonate method when applied to feces and urine, and the ease and rapidity of manipulation recommended it for trial upon substances containing a larger proportion of phosphorus in organic combination.

In comparing the three methods care was taken to secure approximate uniformity in the amounts of samples taken and of reagents used. Of the beef and of the beans about 2 grams were

[1] Bulletin 46, revised edition, Bureau of Chemistry, U. S. Dept. of Agriculture.

[2] Du Bois Reymond's Archiv., physiol. abth., (1897), pp. 552–553 through *Jahr. Thier chemie*, **27**, 643.

taken for each determination; of each of the other samples about 1 gram was used.

The table below shows the results obtained by these three methods upon five of the samples already described (the white of egg being omitted as it contained only 0.1 per cent. of phosphorus, all of which remained in the ash), and on a sample of caseïn prepared in the laboratory and containing less than 0.5 per cent. of ash.[1]

	Percentage of phosphorus found.		
Substance.	Oxygen method.	Carbonate method.	Neumann's method.
Dried lean beef	0.490	0.492	0.499
Dried curd	1.341	1.335	1.327
Caseïn (air-dried)	0.789	0.789	0.797
Yolk of egg	1.364	1.368	1.366
Wheat bran	1 382	1.402	1.393
Beans	0.481	0.470	0.452
Average	0.975	0.976	0.972

The three methods thus yield practically the same results. As shown below it was found that most of the samples lost extremely little phosphorus when burned to ash in the usual manner. It is believed that these samples are fairly representative of ordinary food materials, rich in proteid matter. If so, the determination of phosphorus in food materials is attended with very much less danger of loss than the determination of sulphur.

In the case of the prepared caseïn about seven-eighths of the phosphorus was lost when the material was burned to ash, but in the determination of total phosphorus practically identical results were obtained by the three methods studied, indicating that these three methods are equally applicable to practically ash-free organic compounds of this nature as well as to food materials and ordinary physiological products.

LOSS OF SULPHUR AND PHOSPHORUS IN PREPARING ASH.

The proportion of sulphur which remains in the ash of animal and vegetable substances may not be of much significance in itself, yet as most ash analyses include the determination of sulphates and as the relation of total sulphur to sulphur in ash is being determined in some cases[2] it was thought advisable to include it here.

[1] For this sample the writer is indebted to Mr. P. B. Hawk, of the Department of Physiological Chemistry of this University.

[2] Fraps: This Journal, **23**, 199; **24**, 346.

In the case of phosphorus the loss in preparing the ash is in most cases much smaller and in view of the large number of recorded determinations of phosphorus in the ashes of animal and vegetable materials the relation of this to the total phosphorus becomes a matter of considerable importance.

The percentages of total ash in the air-dried samples, of total sulphur and phosphorus, and of sulphur and phosphorus which remained when the material was reduced to ash in the usual manner,[1] are shown in the following table:

SULPHUR AND PHOSPHORUS REMAINING IN ASH.

Substance.	Total ash. Per cent.	Percentage of sulphur. Total.[2]	Percentage of sulphur. In ash.	Percentage of phosphorus. Total.[3]	Percentage of phosphorus. In ash.
Dried lean beef	2.21	0.813	0.036	0.494	0.457
Dried curd	8.10	0.609	0.072	1.334	1.332
Yolk of egg	4.92	0.821	0.013	1.366	1.307
White of egg	5.22	1.415	0.206	0.105[4]	0.105
Wheat bran	6.58	0.262	0.016	1.392	1.392
Beans	3.02	0.223	0.036	0.468	0.461

Thus while the loss of phosphorus was practically *nil* in four cases and very small in the other two, the loss of sulphur ranged from over four-fifths to practically all of that present.

It should be noted that the sample of curd contained, in addition of some of the salts originally present in the milk, a small amount of sodium acetate, formed by neutralization of the acetic acid used in precipitation, which doubtless aided in the retention of sulphur and phosphorus. As already stated, the sample of prepared caseïn used in the work on phosphorus lost about seven-eighths of its phosphorus on being burned to ash. In the case of the yolk of egg the reduction of the ash to whiteness required two or three hours at the moderate red heat which was used. When the burning was completed over a blast-lamp the ash was reduced to 4.19 per cent., and the phosphorus remaining in the ash to 1.143 per cent. of the original material.

CONCLUSIONS.

For the determination of sulphur the method of combustion in compressed oxygen is preferred. Equally good results were ob-

[1] Bulletin 46, revised edition, Bureau of Chemistry, U. S. Department of Agriculture.
[2] Averages of results by the oxygen and alkali methods.
[3] Averages of results by the three methods used.
[4] Determined by the carbonate method.

tained by the hydroxide-peroxide method but the manipulation is less convenient. The nitric acid method as used gave low results.

In the determination of phosphorus practically identical results were obtained whether the material was oxidized by combustion in oxygen, by heating with carbonate and nitrate, or by boiling with sulphuric acid and ammonium nitrate. For the analysis of food materials and physiological products the last-mentioned method will probably be found most convenient, especially in laboratories where the Kjeldahl method for nitrogen is largely used.

In analyzing animal and vegetable materials there is very much greater danger of loss by volatilization of sulphur than of phosphorus.

The writer desires to express his indebtedness to Prof. W. O. Atwater of Wesleyan University, who encouraged this work in many ways and in whose laboratory a large part of it was done, and to Mr. Emil Osterberg who assisted with many of the determinations.

NEW YORK CITY,
September, 1902.

FURTHER NOTES ON THE BROMINE ABSORPTION OF OILS.

BY PARKER C. MCILHINEY.

Received July 17, 1902.

IN TWO papers published in the Journal of this Society,[1] the writer submitted a method of examining fats and oils in which the substance to be examined was acted upon by bromine dissolved in carbon tetrachloride. The most important advantage claimed for the method was that if the oil or fat contains substances with which bromine reacts to form substitution products, the fact will be made known by the production of a certain amount of hydrobromic acid which is determined in one part of the process. The ordinary animal and vegetable oils and fats, such as olive oil, lard, cottonseed oil, linseed oil, etc., which are practically pure glycerides, absorb almost the whole of the bromine which disappears during its action upon them by direct addition, that is to say, the bromine unites with pairs of carbon atoms which had previously been connected by double or triple bonds, and consequently but

[1] Vol. **16**, 275, and **21**, 1084.

little hydrobromic acid is produced by the reaction. The analytical process gives, for each test made, two figures, one showing the bromine absorbed by direct addition and the other the amount which has substituted hydrogen.

The most frequent adulterants of fatty oils are petroleum and rosin, both of which are relatively cheap. Both of these react with bromine to produce hydrobromic acid, and thereby give very distinct indications of their presence in other oils. An extended application of the process has not resulted in any modifications except in one instance, when we have to deal with a substance which is partly organic and partly inorganic. This condition occurs in boiled linseed oil and more particularly in driers. The oxides of lead and of manganese which are natural constituents of these substances, and also the lime which is sometimes present, neutralize, as might be expected, a part or the whole of the hydrobromic acid, which may be formed by the reaction of bromine with such an adulterant as rosin or petroleum. Consequently when metallic compounds are present it is not safe to assume that an oil is free from rosin simply because its bromine substitution figure is low. If there is any considerable amount of rosin the small amount of lead and manganese present in boiled oil will not obscure the indications, especially as not only is the substitution figure of rosin very high (75 or thereabouts as compared with 3 for linseed oil), but its addition figure is very low, only about 5 as against 105 for linseed oil. On account of the small proportion of driers usually added, it may easily happen, however, that a sample of boiled oil which contains a drier partly composed of rosin or of mineral oil may give bromine figures which are not at all suspicious. If the oil is adulterated with rosin or with mineral oil in larger amounts, 5 per cent. or more, such as would naturally be added if the purpose was to cheapen the product, the lowering of the addition figure will be sufficiently marked to attract attention even if mineral bases are present in sufficiently large amounts to entirely neutralize the hydrobromic acid, and the occurrence of so much mineral base is not likely.

It may be remarked that the iodine figure of rosin is about 0.8 of that of linseed oil, and that the adulteration with rosin may be quite serious without any marked lowering of the Hübl figure.

In the case of the analysis of driers used in making boiled oil, the same remarks apply, but in a much greater degree.

To sum up the matter we may say that the introduction into an oil of mineral bases, such as lime and the oxides of lead and of manganese, decreases the bromine substitution figure given by the oil, and this reduction must be taken account of in the analysis of boiled linseed oil and of driers.

It may be of interest to give some account of the effect of varying conditions upon the results obtained by the process. First with regard to the time required for the contact. A number of experiments have been made to ascertain how long a time is required for the reaction to be completed. It appears, as a result of the experiments, that as far as the reaction of bromine and the pure glycerides is concerned, the reaction goes on to completion in a very short time, probably one minute or less, even in the case of oils absorbing most halogen, such as linseed oil. This appears to be true, generally, providing the absorption is entirely by addition. If part or all of the absorption of halogen is by substitution, the amount absorbed varies, as it is natural to expect that it would, with the time of contact between halogen and the substance. Lewkowitsch[1] takes exception to the author's conclusion that on account of the great variation in the results caused by differences in the time occupied by the experiments, the iodine figure of rosin is of little value as a "constant". He calls attention to the fact that the Hübl figure varies with the time of contact in the case of other substances than rosin. In reply it may be said that in the case of unsaturated glycerides the importance of the time factor is insignificant as compared with its importance when the halogen absorption is mostly by substitution. The writer still feels that the iodine figure of rosin is hardly definite enough to entitle it to recognition as a "constant".

A number of experiments were made to compare the rapidity with which bromine in carbon tetrachloride solution acts upon such a material as common rosin, with the rapidity of the action of Hübl's solution on the same material.

The bromine absorption of a sample of W. G. rosin was determined in four experiments, in one of which the reagent was allowed to act upon the rosin for two minutes, in another for

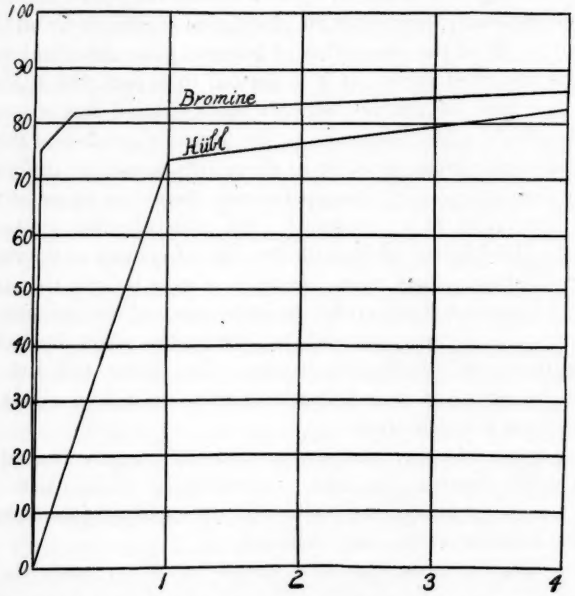
[1] "Oils, Fats, and Waxes," second edition, p. 235.

eighteen minutes, in a third for sixty-nine minutes, and in a fourth for twenty hours; the results were as follows:

Time.	Total bromine absorption. Per cent.
Two minutes	160.8
Eighteen minutes	174.5
Sixty-nine minutes	178.0
Twenty hours	213.4

Similar experiments with Hübl's solution of iodine were previously reported by the author.[1] The same sample of rosin was used in both sets of experiments. The results obtained were as follows:

Time.	Total iodine absorption. Per cent.
One hour	126.7
Two hours	133.1
Four hours	142.0
Eight hours	144.8
Eighteen hours	160.3
Fifty-two hours	172.6



COMPARISON OF RAPIDITY OF ACTION OF BROMINE AND OF HÜBL'S SOLUTION UPON ROSIN.

The two sets of experiments are compared graphically in the

[1] This Journal, 16, 56.

figure. The highest absorption found in each case is taken as 100, the lower absorptions being reduced to the same basis and represented in the figure as ordinates. The abscissas represent time in hours. It will readily be seen from the figure that the absorption of bromine is much more nearly complete at the end of a short experiment than that of iodine in the determination of the Hübl figure, and consequently that the bromine absorption of such a material as rosin is a much more definite figure and less affected by the length of the experiment than the Hübl figure is for the same substance, though by no means a "constant."

Rosin may be taken as one of the best examples of the absorption of halogen purely by substitution, the addition figure being very low indeed, though the total absorption is high.

A series of five experiments, made to determine the effect of varying excess of bromine, gave the following results; a sample of pure linseed oil was used for the experiments:

Percentage of excess of bromine.	Total bromine absorption. Per cent.
16.5	92.4
36.4	95.5
42.1	98.3
81.2	101.0
104.3	103.5

It will be seen that an excess of bromine amounting to 100 per cent. or more of that absorbed by the oil is necessary in order that the reaction may speedily go on to completion.

Another series of experiments was made to determine the effects of varying temperature and of the presence or absence of moisture in the oil. The bromine figure of a sample of linseed oil was determined in four ways:

First, in the ordinary way at the room temperature 20° C.

Second, with 10 cc. of water added to each test at the room temperature.

Third, with 10 cc. of water added to each test and the bottles kept immersed in melting ice.

Fourth, with 10 cc. of water added to each test and the bottles heated to 30° C.

The experiments were all carried on at the same time. The shortest test was eighty-eight minutes and the longest one hundred and eighty minutes.

The results obtained were as follows:

	Total bromine absorption.	Bromine addition.	Bromine substitution.
Dry, ordinary condition.....	110.2	104.8	2.7
10 cc. water, ordinary temperature..	108.6	104.0	2.3
10 cc. water, cooled	109.8	104.0	2.9
10 cc. water, heated	113.2	103.0	5.0

It is noteworthy that the results appear to be but slightly affected by the variations introduced and particularly that the presence of water seems to be without serious effect.

FIXATION OF PHOSPHORIC ACID IN THE SOIL.

By J. T. Crawley.

Received June 11, 1902.

It has been known for a long time that when soluble phosphates are applied to the soil, they become fixed by the bases, lime, iron, etc., and are not leached from the soil to any very considerable extent by rain or irrigation waters. By this process water-soluble phosphoric acid is "reverted" or changed to a combination not soluble in water. This is akin to the fixation of potash and ammonia, which are changed into insoluble combinations in the soil.

This is a wise provision of nature and prevents salts and bases in the soil which have been rendered soluble by weathering and other agencies from being washed out and lost from the soil; and it enables the agriculturalist to apply certain forms of soluble fertilizers to growing crops without fear of losing them in the drainage waters. But what becomes of the water-soluble phosphoric acid applied as a fertilizer; is it fixed near the surface, or is it well distributed throughout the soil where the roots of plants can get it?

The following investigation was undertaken for the purpose of determining to what extent water-soluble phosphoric acid is distributed through the soil before it becomes fixed. In certain sections of these islands the cane grows by irrigation; in other sections the rainfall is ample. Where irrigation is practiced the soluble fertilizer is scattered along the cane row, in some cases covered, in other cases not, and followed up within a day or two by irrigation. Three or four inches of water would represent an

average irrigation. Usually the water disappears in the soil within twenty or thirty minutes of application. Where rainfall is depended upon, fertilizers are covered up.

APPARATUS AND METHODS.

The most conclusive and determinate method would be to apply phosphoric acid in water solution to the soil, and then, by making analyses of the soil, find where it has been fixed. This, however, is not practical since our chemical methods are not sufficiently delicate to detect slight differences in the amount of this acid, and were a soil analyzed before and after the application of an ordinary dose of phosphoric acid, this amount would not be detected. The lysimeter method is the next best; a given weight of phosphoric acid is applied to the soil, followed by an excess of water, the drainage water caught and analyzed. The difference between the amount of acid applied and that found in the drainage is the amount abstracted and held by the soil. By varying the depth of soil in this experiment we find the depth at which the phosphoric acid is held. Boxes, 9 in. cube, were made, several holes bored in the bottom for the purpose of allowing the drainage water to escape, and varying depths of soil placed in them. Ten grams of double superphosphate were applied in each case, which is as large an amount as is applied in the cane rows to a space 9 inches by 9 inches. In each case 4800 cc. of water were added, this amount being probably an average irrigation. Notes were made of the time necessary for the water to percolate through the soil, and the total time of draining.

RESULTS.

I. Experiments with dark-colored soil from Makiki. This soil contains more phosphoric acid soluble in weak vegetable acid solutions than any other Hawaiian soil thus far examined.

(1) Six inches of soil; water began percolating through the bottom of the soil at end of six minutes, and 1790 cc. of water were recovered within one-half hour, when drainage was practically completed. The 1790 cc. of water contained 0.023 gram P_2O_5 or 0.57 per cent. of total applied.

(2) Six inches of soil; the phosphate was covered up in the moist soil and allowed to stand over night. Water began drain-

ing within two minutes, and 3300 cc. were drained in forty minutes, containing but a trace of phosphoric acid.

II. Typical red soil from the Honolulu plantation.

(1) Six inches of soil; water began draining in two minutes, and finished draining in forty minutes. Recovered 2072 cc. water containing 0.1113 gram P_2O_5 or 2.78 per cent. of total applied.

(2) Six inches of soil containing 20.72 per cent. moisture; phosphate covered up and allowed to stand over night; began draining in three minutes; finished draining in fifty minutes. 2320 cc. of water were recovered, containing 0.0134 gram P_2O_5 or 0.34 per cent. of total applied.

(3) Three inches of soil; began draining in one minute; finished draining in thirty minutes. Recovered 3130 cc. of water containing 0.35 gram P_2O_5 or 8.75 per cent. of total applied.

(4) Three inches moist soil; phosphate covered up and allowed to stand over night. 2886 cc. of water were recovered, containing 0.0408 gram P_2O_5 or 1.02 per cent. of total applied. The soil and phosphate were allowed to stand two days. Two liters of water were poured over it, of which 1700 cc., containing 0.0048 gram P_2O_5 or 12 per cent. of total applied, were recovered. After standing two days this was subjected to a further leaching, the drainage containing but a trace of phosphoric acid.

(5) One inch of soil; began draining in ten seconds; finished draining in nine minutes. Recovered 4260 cc. water containing 1.866 grams P_2O_5 or 46.65 per cent. of total applied.

(6) One inch of soil; phosphate covered up and allowed to stand four hours before irrigation. Drainage water contained 0.274 gram of P_2O_5 or 6.85 per cent. of total applied.

(7) One inch of soil; phosphate covered up and allowed to stand over night. Drainage contained 0.2928 gram P_2O_5 or 7.32 per cent. of total. Same after standing two days and washing with two liters of water, yield 0.033 gram P_2O_5 or 0.82 per cent of total.

Putting these results in tabulated form we have:

TABLE I.—SHOWING THE AMOUNT OF PHOSPHORIC ACID HELD BY THE SOIL.

Depth of soil. Inches.	Black soil, when irrigated.	P_2O_5 retained. Per cent.	Red soil, when irrigated.	P_2O_5 retained. Per cent.
6	Immediately	99.43		....
6	After fifteen hours	100.00		....
6	....	....	Immediately	97.22
6	....	....	After fifteen hours	99.66
3	....	....	Immediately	91.25
3	....	....	After fifteen hours	98.98
3	....	....	Same after two days	99.88
1	....	....	Immediately	53.35
1	....	....	After four hours	92.68
1	....	....	After fifteen hours	99.18
			Same after two days	....

From this we see that when the application of the fertilizer is followed immediately by irrigation, (1) more than one-half the phosphoric acid remains in the first inch of soil, more than nine-tenths in three inches, and practically the whole within six inches of the surface; (2) when an interval of fifteen hours intervenes between the application and the irrigation, more than nine-tenths of the phosphoric acid is retained by the first inch of soil and practically the whole by the first three inches. These conclusions are rather startling, inasmuch as it has been heretofore believed that water-soluble phosphoric acid, when applied to the soil, becomes pretty well distributed throughout the first eighteen inches or two feet of the soil when it is easily accessible to the roots of the plants. This bears on the question of the relative value of water-soluble and so-called citrate-soluble or "available" phosphoric acid. At the various experiment stations in the United States the same or very nearly the same valuation is put upon the two forms. Where there is a difference it is rarely more than 1 cent. per pound in favor of the water-soluble. Certainly on Hawaiian soils where the phosphoric acid becomes reverted at the surface, or very near the surface, the two forms have very nearly the same value, for even under the most favorable circumstances the water-soluble phosphates are disseminated throughout the soil but sparingly. On the other hand, in cases where fertilizers are applied and covered up a few hours before irrigation practically all of the phosphoric acid becomes reverted and remains near the surface. Also on plantations depending on rainfall where the fertilizers are applied and covered up, water-soluble and reverted

phosphoric acid have practically the same value, as the water-soluble becomes reverted and subsequent rains cannot wash it down to the roots of the plants, nor disseminate it throughout the soil. This is a possible explanation of a fact which I have set forth in former papers; namely, that phosphates have not shown as good results on Hawaiian soils as the other fertilizer ingredients —nitrogen and potash. It takes considerable cultivation to disseminate the phosphates throughout the soil, and although they may be deficient, yet an application is not followed by the immediate results that the planter expects.

Seeing that the water-soluble phosphoric acid is taken up so readily, a further experiment was made to determine the *total capacity* of the soil to fix phosphoric acid. 800 grams of red soil and 50 grams of double superphosphate containing 20.58 grams water-soluble phosphoric acid were thoroughly mixed together. This mixture was kept moist to promote the chemical action, and samples were withdrawn from time to time to estimate the water-soluble acid.

March 26th, 800 grams soil and 50 grams double superphosphate mixed; March 27th, 41.6 per cent. of P_2O_5 had become fixed; March 29th, 57.7 per cent. of P_2O_5 had become fixed; April 3rd, 73.0 per cent. of P_2O_5 had become fixed; April 17th, 85.65 per cent. of P_2O_5 had become fixed.

Or, taking 3,500,000 pounds as the weight of one acre of soil to the depth of 1 foot, we find that this soil absorbed:

After one day 35,235 pounds P_2O_5 per acre to depth of 1 foot; after three days 48,872 pounds P_2O_5 per acre to depth of 1 foot; after eight days 61,431 pounds P_2O_5 per acre to depth of 1 foot; after twenty-two days 72,545 pounds P_2O_5 per acre to depth of 1 foot.

This latter figure would represent all the phosphoric acid in 181 tons of acid phosphate.

These astonishing figures lead to a consideration of the nature of the soils experimented with, and the reason for the rapid and great fixation of phosphoric acid by Hawaiian soils. On p. 99. *et seq.*, of Maxwell's "Lavas and Soils of the Hawaiian Islands" will be found a comparison of Hawaiian and American soils, in which it is shown that Hawaiian soils are very much more basic than American soils.

TABLE II.

Soils.	Basic constituents. Per cent.	Acid constituents. Per cent.
Hawaiian	63.717	36.458
American	18.980	81.014

Whereas the American soils from which these figures were drawn contain but 13.250 per cent. iron and aluminum oxides, the Hawaiian soils contain 59.24 per cent.

All Hawaiian soils are very basic, and these bases are probably in a condition to seize at once the phosphoric acid and hold it. The American soils being much older than Hawaiian soils the soluble bases have been washed out, the soils are less basic in character, and will probably hold very much less phosphoric acid than the Hawaiian soils. Following is an average of a number of analyses of dark red soils, and the soil from the Honolulu plantation would not differ very materially from these figures.

TABLE III.—DARK RED SOILS.

	Per cent.
Insoluble matter	37.20
Moisture	6.16
Combustible matter	11.33
TiO_2	2.59
P_2O_5	0.19
SO_3	0.31
CO_2	0.18
CaO	0.34
MgO	0.44
Fe_2O_3	22.94
Al_2O_3	16.84
Mn_3O_4	0.42
K_2O	0.39
Na_2O	0.75
	100.08

With soils of this general composition it would be strange if their absorptive power of phosphoric acid were not great.

HONOLULU, H. I.

THE ESTIMATION OF SOIL ACIDITY AND THE LIME REQUIREMENTS OF SOILS.

By F. P. Veitch.

Received August 15, 1902.

Within the past few years, it has been definitely shown that the reaction of a soil exerts a marked influence on its crop-producing power. While the reaction affects the chemical and the physical condition of the soil to a considerable extent, the growth of plants is more directly affected by the action of the acids on the plant roots, and upon the micro-organisms of the soil.

The importance of the matter has led to the elaboration of several methods for determining the amount of acids in soil, but, owing to the exceedingly small amount usually present in ordinary arable soils, the influence of other material, and the constant changes taking place in the soil, none of these methods has shown a close relation between crop production and the amount of acidity as determined by any of the methods. Wheeler, Hartwell, and Sargent[1] have recently made a critical examination of the methods which have been proposed for this purpose, checking the chemical methods by field experiments. The investigators were unable to correlate the chemical results obtained by any of the methods examined with the field results, but regarded as promising the titration of dilute ammonia which had been in contact with the soil for some time, and also a method based on the evolution and estimation of the carbon dioxide freed from calcium carbonate by the acid soil on boiling them together in water.

It has not seemed advisable to the writer to give more study to either of these methods, because any solution placed in contact with a soil, no matter whether acid or alkaline, will be decreased in strength through adsorption or physical reaction between the solution and the soil; and we have no certain means of measuring the amount thus adsorbed. Further, owing to the deflocculating power of ammonia, it is practically impossible to get even an approximately clear filtrate or supernatant liquid, and the amount of acid as determined is more or less affected by this fact. With regard to the evolution and estimation of carbon dioxide, the

[1] This Journal, **22**, 153.

evolution continues indefinitely, and whether it is due to reaction between the soil and the carbonate or to the oxidation of the organic matter of the soil is not definitely known, though it is probable that it is more largely due to the first-mentioned reaction.

After a great deal of experimenting the writer has devised a method in which lime-water is used to neutralize the acid material in the soil. The method is based on the fact that the small excess of lime-water present, after the neutralization of the acid material, is converted into carbonates and bicarbonates, the boiling solution of which gives an alkaline reaction with phenolphthaleïn.

No effort has been made to secure great refinement or close duplication of results, because the problem is a practical one in which the application of several hundred pounds of lime, more or less, per acre has but little economic or agricultural significance. It may be said, however, that the writer has reason to believe that the method will give duplicate results accurate to one hundred pounds of lime per acre foot of 3,500,000 pounds. The method is as follows:

For the preliminary test, to three portions of 10 grams each of the soil in platinum dishes add 50 to 60 cc. of distilled water, and different amounts of standard lime-water. For example, to the first 10 cc., to the second 20 cc., and to the third 30 cc. of lime-water are added. Dry down at once on the steam-bath, transfer to a stoppered Jena flask with 100 cc. of distilled water, allow to stand over night, with occasional shaking, filter (the filtrate should be clear or but faintly turbid), take 50 cc. in a Jena beaker, add a few drops of phenolphthalein solution, and boil until the appearance of the pink color, or in the case where no color is developed to a volume of about 5 cc. Then with the two portions of treated soil, one of which has been rendered alkaline by the added lime-water and the other of which is still acid, as guides, prepare three fresh portions of 10 grams each, and add lime-water as before, except that the amount added to a dish differs from that added to another, by only one or two cc. Dry, allow to stand, filter, and treat exactly as before; the smallest amount of lime-water which gives the characteristic pink with phenolphthaleïn is taken as the acidity equivalent of the soil. From the data thus obtained, the acidity and lime requirements of the soil may be calculated.

The results which have been obtained with this method are given in Table I. The amount of lime (CaO) required to neutralize the acids in an acre foot of 3,500,000 pounds is also included. 1 cc. of calcium hydroxide to 10 grams of soil is approximately 450 pounds of lime per acre.

TABLE I.

		50 cc. filtrate boiled.		
		Acid with cc. $Ca(OH)_2$.	Alkaline with cc. $Ca(OH)_2$.	Lime (CaO) required per acre foot of 3,500,000 pounds.
No. 1	Summit, R. I	20	25	11,250
No. 2	Jamestown, R. I	..	8	3,600
No. 3	Harrisville, R. I	10	15	6,750
No. 4	Foster Center, R. I	25	32	14,300
No. 5	Niantic, R. I	6	8	3,600
No. 6	South Portsmouth, R. I	30	35	15,750
No. 7	Hamilton, R. I	17	18	8,100
No. 8	Slocumville, R. I	54	56	25,200
C	Coarse sand used in greenhouse	3	4	1,800
No. 1	A. O. A. C. sample 1900	9	10 10	4,500
No. 3	A. O. A. C. sample 1900	50	52 52	22,500
No. 4	A. O. A. C. sample 1900	..	1	450
No. 3	A. O. A. C. sample 1901	8	9	4,050
No. 4	A. O. A. C. sample 1901	1	2	900
No. 5	A. O. A. C. sample 1901	1	2	900
5118	Leonardtown loam, Md	4	5 5	2,250
5127	Leonardtown loam, Md	8	10	4,500
5112	Norfolk loam, Md	4	5	2,250
5131	Norfolk sand, Md	0	1	450
4244	Conowingo Barrens, Md	4	5	2,250
3624	Fine sandy soil, Fla. (much organic matter)	7	8	3,600
A	Gabbro soil, Md	10	12 12	5,400
O	Lime Expt. plot, Md. Station, 60 bushels per acre	1	2	900
B	Lime Expt. plot, Md. Station, no lime	5	6 6	3,150
D	Md. phosphoric acid plots	1	2 2	900

The samples from Rhode Island Nos. 1 to 8 are samples kindly furnished by Dr. Wheeler, and are the same upon which he worked in the investigation previously referred to. Owing to the

scarcity of material, closer readings than those given in the table could not be made, on these samples; but the readings made on other samples show that much closer readings could probably have been made here.

A summary of Wheeler's results on these soils, field and laboratory, is given in Table II. To this has been added the results obtained by the lime-water method on these same samples by the writer. For a more satisfactory comparison, the lime-water results have been calculated to their nitrogen equivalents, and the acidity of the samples as expressed in pounds of lime (CaO) per acre foot of 3,500,000 pounds has been included.

These results, while somewhat unsatisfactory, are not so surprising when we consider the different soils and the number of factors involved in plant production which are influenced and modified by the addition of lime to a soil, even though that soil may be liberally supplied with available plant food. It is of interest to note that soils Nos. 6, 8 and 9 produced such large crops of beets after liming, although the soils still remained very acid. In other words, after liming, beets were not as sensitive apparently to an acidity equivalent to 20,000 pounds of lime per acre as they were to half this amount on unlimed, but different soils, a fact which possibly indicates that the toxic effect of acids is not so great in the presence of large quantities of soluble lime-salts.[1] This fact is highly important practically and may explain why small applications of lime are often as beneficial as large. It may also explain why slightly acid soil will often produce certain crops, clover, for instance, which will not grow on other soils which are even less acid.

It is also interesting to note that the relative acidity of these soils is the same, whether determined by treatment with ammonia, as was done by Wheeler, or by treatment with lime-water, as was done in this laboratory.

Perhaps the most striking point brought out in the table is the apparent relation of alkali neutralized by the soil to the total humus of the soil. While this relation does not seem to be exceedingly close, it is clearly apparent and is very suggestive in lending support to the hypothesis that the acidity of soil is gener-

[1] *Vide* Ninth Annual Report R. I. Expt. Station p. 309; also Report 71, Bureau of Soils, U. S. Dept. of Agriculture.

TABLE II.—COMPARISON OF THE AMMONIA WATER, AND THE LIME-WATER METHODS.

Summarized from Wheeler's results.

	Yield of beets unlimed. Pounds per 1/20 acre.	Yield of beets limed. Pounds per 1/20 acre.	Increase due to liming. Pounds.	Total humus. Per cent.	Mgs. N in NH_3 retained by 10 grams soil.	Mgs. CaO retained by 10 grams soil lime-water method.	Mgs. N equivalent to CaO retained by 10 grams soil.	CaO required per acre foot to render the soil neutral. Pounds.	CaO still required per acre foot to render soil neutral after Wheeler's liming. Pounds.
No. 1 Summit, R. I.	47.4	92.9	45.5	1.73	19.6	32.0	16.0	11,250	6,250[1]
No. 2 Jamestown, R. I.	75.8	152.7	76.9	0.85	10.4	10.2	5.1	3,600	....
No. 3 Harrisville, R. I.	151.5	207.3	55.8	1.46	14.1	19.2	9.6	6,750	1,750
No. 4 Foster Center, R. I.	36.3	143.4	107.1	2.21	25.5	40.9	20.4	14,300	9,300
No. 5 Niantic, R. I.	9.9	43.4	33.5	0.95	7.9	10.2	5.1	3,600	....
No. 6 South Portsmouth	26.0	153.0	127.0	2.63	27.2	44.8	22.4	15,750	10,750
No. 7 Hamilton, R. I.	14.5	131.8	117.3	1.60	15.8	23.0	11.5	8,100	3,100
No. 8 Slocumville, R. I.	1.0	101.8	100.8	5.08	43.8	71.5	35.75	25,200	20,200
No. 9 Kingston, R. I.	6.6	161.4	154.8	5.15	36.1	66.6	33.3	23,400	18,400

[1] The figures in this column were obtained by subtracting the pounds of lime (CaO) applied to duplicate plots by Wheeler, from the figures given in the preceding column.

ally due to organic acids. In studying these figures, the fact should be borne in mind that neither the methods of determining acidity nor total humus are very exact, and there may be errors in these various determinations, which, if eliminated, would make the relation pointed out much more striking.

As with all other chemical methods used in soil work, the method must not only give accurate results, but these results must have an agricultural significance. Let us see how well the proposed method satisfies the conditions.

The development of the pink color with phenolphthaleïn in the boiled aqueous extract of a soil is doubtless only a question of the volume of extract which is boiled down; even very acid soils will, on long-continued treatment with much water, yield an extract which, on concentration, will give an alkaline reaction with this indicator. A great number of determinations made in this laboratory shows that a soil which gives an alkaline reaction with litmus paper also gives an aqueous extract which is alkaline to phenolphthaleïn when treated with water in the proportion of 1:10, and 50 cc. of the extract is boiled. Numerous determinations of the reaction of soils from all over the country indicate very strongly that those soils which are alkaline to litmus and to phenolphthaleïn under the conditions above described are always more productive soils than contiguous soils which are acid to these indicators. These are the reasons why the proportion of soil to water, and the amount of filtrate to be boiled, as given above, were adopted.

As has been said, we have no method by which we can determine how much of the lime taken up by the soil is actually neutralized by the acid material of the soil, and how much is simply adsorbed and held physically by the soil in such a manner that it does not pass into solution. This is the chief difficulty inherent in any titration method for determining soil acidity. Plus errors are thus introduced, and the acidity of a soil appears greater than it actually is. Experiments, in which soils of different nature were treated with known amounts of dilute ammonia (N/20), soda (N/50), and lime-water (N/20), and aliquot portions of the filtrate titrated both directly with acid, and also by adding an excess of acid and titrating back, showed in every instance that the amount of adsorbed alkali was greater than by the lime-water method. The figures in Table II show the same thing.

Theoretically, there is every reason to believe that adsorption is less under the conditions obtained in the lime-water method than in the titration methods, for, as we know, adsorption is actually greater from the more concentrated solution, and in the titration methods we must always expect to have more alkali present than is sufficient to neutralize the acid material of the soil, and to satisfy the soil's adsorptive power in the presence of such excess of alkali.

In the method above outlined, the amount of alkali which must be present is enough to neutralize the acid material plus a little more than the soil is able to hold against the solvent power of partially carbonated water. That this is so seems quite clear, and is strongly supported by the results in Table II, from which we see that in every case the lime equivalent to nitrogen retained by the soil is much less by the lime-water than by the ammonia-water method. The differences are much too large and regular to be accounted for either by errors or by differences due to neutralization of the acid material of the soil. Another point: It is more than likely that considerable reaction takes place between the non-acid material of the soil and ammonia, even in the cold. If there is any reaction between the lime-water and the material, it is reasonable to think that it is much less, because the very small excess of lime-water is immediately converted into carbonate and bicarbonate, as shown by the behavior toward phenolphthalein. Nevertheless we must regard all these methods as likely to give high results, owing to the probable combination of the alkalies with some silica and silica compounds, both reactions introducing plus errors. The smallest difference between the two methods occurs on No. 5, which is visibly a coarse sandy soil, and upon which adsorption would be expected to be at a minimum.

Reference has been made to the fact that Wheeler regarded as particularly promising a method based on the evolution of carbon dioxide from a mixture of soil and calcium carbonate in boiling water. He found that after boiling such a mixture (40 grams of soil and 4 grams of calcium carbonate) until apparently the evolution had become constant and hence the evolution of carbon dioxide set free by the acid material in the soil had ceased, that two more boilings of the same mixture yielded 0.016

and 0.048 gram of carbon dioxide. These results indicate the decomposition of calcium carbonate equal to 20.8 and 16.6 mg. of lime to 40 grams of soil. These figures are equal to 4.4 and 3.4 cc. of lime-water to 10 grams of soil. From this it would appear that the possible errors would be greater by this method than by the lime-water method.

As has been pointed out, in all these methods the possible combination of the lime with silica and other inorganic soil constituents, without the release of an equivalent of some other base, is a source of error which increases the actual acidity of the soil. Any difference in the methods in this particular would probably be in favor of the lime-water method. As a matter of fact, the adsorption of the added alkali appears to introduce no error greater than the working limits of the method, a fact which was shown by determining the acidity of two soils in natural condition, and also after they had been powdered. On the other hand, adsorption phenomena certainly vitiates the results by those methods based on the titration of an aqueous extract of the soil or of an alkali which has been in contact with the soil. Nor does it seem probable that the water-insoluble material of an acid nature produces an appreciable error in the method, there being every reason to suppose that these materials will be neutralized by the lime. Further, it is believed that under the conditions of the method, the results are not complicated by the reaction of free carbonic acid or by bicarbonates.[1] Viewed in any light, this method or any method based on the use of lime-water or lime carbonate as the neutralizing agent, must appear to one as being along the right line, imitating as it does actual field conditions.

Analytically considered, the method appears to be sufficiently reliable for practical purposes, and appears to be the best now available for the end in view.

Agriculturally considered, we have no positive direct data showing that the acidity of a soil as determined by analytical methods has a definite ratio to the crop production of that soil. The fact that those soils which are universally regarded as fertile, have an alkaline reaction to litmus paper and to phenolphthalein, when their aqueous extracts are boiled, as in the previously de-

[1] The data upon which this view is based will be given in full in a publication soon to appear from the Bureau of Soils, U. S. Dept. of Agriculture.

scribed method, furnishes strong evidence as to the agricultural significance of the results thus obtained, but so far no one has been able to show a close agreement between crop yields and the lime requirements of soil as determined by laboratory methods.

BUREAU OF SOILS, DEPARTMENT OF AGRICULTURE, WASHINGTON, D. C.

THE ANALYSIS OF VANILLA EXTRACT.

BY A. L. WINTON AND M. SILVERMAN.

Received August 11, 1902.

HESS AND PRESCOTT, in papers published in this Journal,[1] have discussed the adulteration of vanilla extract and have described methods devised by them for the separation and determination of vanillin and coumarin, for the distinction of genuine from artificial extracts, and for the detection of artificial coloring-matter, all of which methods, with slight changes, are included among the "Provisional Methods for the Analysis of Foods", adopted by the Association of Official Agricultural Chemists.[2]

Preliminary to the examination of commercial extracts, under the Connecticut pure food law, we have subjected these methods to a critical investigation, the results of which, while substantiating in the main the accuracy of the methods, suggested certain modifications. The Hess and Prescott method for determination of vanillin and coumarin was found to be thoroughly reliable but susceptible of abridgment without diminishing its accuracy.

The methods as finally amended were employed in the analysis of five extracts made in the laboratory and sixty-two commercial extracts.[3]

METHODS OF ANALYSIS.

Determination of Vanillin and Coumarin. Modified Hess and Prescott Method.—The modified method differs from the original method in three details:

First. Two per cent. instead of 10 per cent. ammonia is used, and consequently a less concentrated ammonium chloride solution is obtained after neutralizing with hydrochloric acid, thus reducing the chance of carrying this salt into the extract.

[1] Vol. **21**, 256, 721.
[2] Bulletin 65, U. S. Dept. Agr., Bureau of Chem., pp. 69–71.
[3] Conn. Agr. Expt. Sta., Rep. 1901, pp. 152–162.

Second. A greater bulk of ammonia is used, to diminish the error due to possible mechanical loss during shaking.

Third. The vanillin and coumarin are weighed after evaporation of the ether solutions, whereas in the original process they are not weighed until they have been redissolved in petroleum ether and again evaporated. This procedure not only materially shortens the process, but avoids the errors due to crawling of the solutions while redissolving and reevaporating. Any matter insoluble in the petroleum solvent is afterwards weighed with the dish and a correction introduced, but if care is exercised in the separation, this residue is insignificant. The evaporation of the petroleum extract is, however, necessary if melting-points are to be determined, but this evaporation can go on at leisure after obtaining the quantitative results.

A full description of the method follows:

Dealcoholize 25 grams of the extract in an evaporating dish upon a water-bath, at a temperature of about 80° C., adding water from time to time to retain the original volume. After removal of the alcohol, add normal lead acetate solution, drop by drop, until no more precipitate forms. Stir with a glass rod to facilitate flocculation of the precipitate, filter through a moistened filter, and wash three times with a few cubic centimeters of hot water. Cool the filtrate and extract with ether by shaking out in a separatory funnel. Use 15 to 20 cc. of ether at each separation, repeating the process three or four times, or until a few drops of the ether, evaporated upon a watch-glass, leave no residue. Place the combined ether extracts containing all of the vanillin and coumarin in a clean separatory funnel, and shake out four or five times with 2 per cent. ammonia, using 10 cc. for the first shaking, and 5 cc. for each subsequent shaking.

Set aside the combined ammoniacal solutions for the determination of vanillin.

Wash the ether solution into a weighed dish, and allow the ether to evaporate at the room temperature. Dry in a desiccator and weigh. Usually the dried residue is pure coumarin. Treat the residue with 5 to 10 cc. of cold petroleum ether, boiling between 30° and 40° C. and decant off the clear liquid into a beaker. Repeat the extraction with petroleum ether until a drop, evaporated

on a watch-glass, leaves no residue. Dry the dish for a few moments in a water-oven, cool and weigh. Subtract the weight of the dish and the residue (if any) from the weight previously obtained after evaporation with ether, thus obtaining the weight of pure coumarin. Allow the petroleum ether to evaporate at the room temperature, and dry, if necessary, in a desiccator. The residue should be crystalline and have a melting-point of 67° C. This, with the characteristic odor of coumarin, is sufficient for its identification.

Slightly acidulate the ammoniacal solution reserved for vanillin with 10 per cent. hydrochloric acid. Cool and shake out in a separatory funnel with four portions of ether as described for ether extraction. Evaporate the ether at room temperature in a weighed platinum dish, dry over sulphuric acid, and weigh. Treat the residue with boiling ligroin (boiling-point, 80° to 85° C.), decanting into a dry beaker. Repeat the treatment until all vanillin is removed. Dry the dish with residue (if any) for a few moments at 100° C. and weigh. Subtract the weight from the weight previously obtained after evaporating the ether. The difference is the weight of vanillin. Evaporate the ligroin at room temperature and dry in a desiccator. The residue should be crystalline, have a melting-point of 80° to 81° C. and have the characteristic odor and crystalline form of vanillin.

Hess and Prescott,[1] as a test of their process, determined vanillin and coumarin in two 25-gram portions of vanilla extract U. S. P., to each of which had been added 0.5 gram of pure coumarin. The following are their results: Vanillin (I), 0.3081 gram; (II), 0.2997 gram.[2] Coumarin (I), 0.4910 gram; (II), 0.4820 gram. These figures illustrate the accuracy of the process for determination of coumarin, but throw no light on its value for determination of vanillin, as the amount present was unknown.

As a further test of the Hess and Prescott method, we have made determinations in 25-gram portions of a solution containing the same amount of sugar and alcohol as vanilla extract U. S. P., to which weighed quantities of pure vanillin and coumarin had been added, proceeding as follows:

[1] This Journal, **21**, 256.

[2] Owing probably to a typographical error, these amounts are about ten times what are usually present.

Method *A*. The original Hess and Prescott method, using ether in all extractions and 10 per cent. ammonia for separation of vanillin and coumarin.

Method *B*. Same as *A*, except that chloroform was substituted in all cases for ether.

Method *C*. Same as *A*, except that chloroform was used in the extraction of vanillin from the ammonia extract.

Method *D*. The modified method used by us, as already described.

In each case the separated vanillin and coumarin was weighed after the evaporation of the ether or chloroform (first evaporation), and only in a few instances was it reweighed after dissolving in the petroleum solvent and reevaporating (second evaporation). The results follow:

RESULTS OBTAINED BY VARIOUS MODIFICATIONS OF HESS AND PRESCOTT'S METHOD, ON MIXTURES CONTAINING KNOWN QUANTITIES OF VANILLIN AND COUMARIN.

	Vanillin.			Coumarin.		
Method.	Taken. Gram.	Found after first evaporation. Gram.	Found after second evaporation. Gram.	Taken. Gram.	Found after first evaporation. Gram.	Found after second evaporation. Gram.
A	0.0120	0.0101	0.0100	0.0170	0.0162	0.0165
B	0.0695	0.0723	0.0705	0.0975	0.0902	0.0900
C	0.0495	0.0490	.....	.....	.....	.....
C	0.0280	0.0261	.....	.....	.....	.....
C	0.0610	0.0630	0.0575	0.0855	0.0751	0.0740
C	0.0120	0.0136	0.0120	0.0170	0.0160	0.0162
C	0.0290	0.0280	.....	.....	.....	.....
C	0.0495	0.0455	.....	.....	.....	.....
D	0.0625	0.0636	0.0610	0.0875	0.0800	0.0786
D	0.0625	0.0620	.....	0.0875	0.0796	.....
D	0.0625	0.0621	0.0585	0.0875	0.0803	0.0795
D	0.0625	0.0602	.....	0.0125	0.0125	.....
D	0.0625	0.0630	.....	0.0125	0.0124	.....
D	0.0625	0.0615	.....	0.0125	0.0122	.....

From these figures it is evident that the process, both as originally described and as abbreviated by us, gives remarkably accurate results for vanillin and sufficiently accurate results for coumarin.

Where the amount of coumarin was large, there was an unac-

countable deficiency of this substance, but for the amounts present in extracts, which, in our experience, has not exceeded 0.0600 gram per 25 grams of extract, the method is all that could be desired. The melting-points of the coumarin and vanillin in all cases were close to the theory.

Without doubt, this excellent method is in all points the best that has yet been devised.

Tests for Caramel, Coal-tar Dyes, etc.—Valuable indications of the nature of an extract are obtained in the process of determination of vanillin and coumarin. Pure extracts of vanilla beans give, with lead acetate, a bulky, more or less glutinous, brown-gray precipitate, and a yellow or straw-colored filtrate, whereas purely artificial extracts colored with caramel give a slight, dark brown precipitate and a dark brown filtrate. If both vanilla bean extract and caramel are present, the precipitate is more or less bulky and dark-colored, and the filtrate is more or less brown. The solution remaining after extraction of the vanillin and coumarin with ether, if dark-colored, should be tested both for caramel and coal-tar colors.

In our experience the most satisfactory test for caramel is to shake with fullers' earth as recommended by Crampton and Simons.[1] If the color is due to caramel and a grade of fullers' earth is used, which experience has proved suitable, the solution, after filtering, is yellow or colorless. This test does not positively identify the color, as some other brown substances may give similar reactions, but no such substance is liable to be present in vanilla extract.

Amthor's test[2] for caramel has not given in our hands decisive results, and Hess' test,[3] owing to the formation of caramel from the sugar of the extract during the heating with acid, has given reactions in extracts known to contain none whatever of this substance.

Coal-tar dyes may be tested for by Arata's method.[4]

Determination of Total Residue.—Introduce into a flat-bottomed aluminum dish 10 grams of ignited sand and a short stirring-rod,

[1] This Journal, **21**, 355; **22**, 810.
[2] *Ztschr. anal. Chem.*, **24**, 30.
[3] This Journal, **21**, 721.
[4] *Ibid.*, **22**, 582.

and weigh. Add 5 grams of extract and heat on a boiling water-bath, with constant stirring, until the bulk of the water is removed. Dry in a water-oven until the loss sustained in one hour is less than 2 mg.

The "total residue" not only includes the total solids, but also glycerin which is often present in such amount that the residue appears moist after drying. Owing to the slow evaporation of this substance, absolutely constant weight can not be secured but the loss is so gradual that the above method is usually sufficiently accurate.

Determination of Alcohol.—Dilute 25 grams to 150 cc. and distil into a 100 cc. pycnometer. Determine the specific gravity of the distillate at 15.5° C. and calculate the percentage by weight.

Determination of Cane-Sugar. Detection of Glucose.—Dissolve 13.024 grams (one-half the normal weight) of the material in about 80 cc. of water. Add 3 cc. of basic lead acetate and 2 cc. of alumina cream, make the volume up to 100 cc. and filter through a dry filter. Determine the rotatory power of the solution in a 200 mm. tube. To 50 cc. of the filtrate referred to above, add 5 cc. concentrated chemically pure hydrochloric acid. After thorough mixing, place in a cold water-bath and heat quickly to 68° C. After standing at that temperature for ten minutes, cool quickly, filter from lead chloride, if necessary, and examine in a 220 mm. tube, first at the room temperature and finally at 86° C.

Estimate the percentage of cane-sugar by Clerget's formula. A considerable plus reading at 86° shows the presence of glucose.

Determination of Glycerin.—Determine in 5 grams of the extract as directed for sweet wines.[1]

ANALYSES OF GENUINE AND ARTIFICIAL VANILLA EXTRACTS.

Five extracts were made in the Station laboratory, from different grades of beans, after the U. S. P. formula.

An extract of tonka beans was also prepared in the laboratory in the same manner as the vanilla extracts, substituting, however, tonka beans for vanilla beans.

Analyses of these extracts and of fourteen representative commercial extracts, both pure and adulterated, are given in the table:

[1] Borgmann: Anleitung zur Chem. Analyse des Weines, 2 Auf., p. 50. U. S. Dept. of Agr. Div. of Chem., Bull. 46, Revised ed., p. 63.

ANALYSIS OF VANILLA EXTRACTS.

Serial No.		Vanillin.	Coumarin.	Total residue.[1]	Cane-sugar.	Glycerin.	Solids other than cane-sugar.	Alcohol by weight.	Coloring.
4562	U. S. P. Mexican beans	0.13	0.00	22.60	19.90	0.00	2.70	37.96	natural
4561	U. S. P. Mexican beans (cut)	0.07	0.00	23.10	19.20	0.00	3.90	39.92	"
4504	U. S. P. South American beans	0.22	0.00	22.00	19.00	0.00	3.00	38.58	"
4505	U. S. P. Bourbon beans	0.14	0.00	23.13	20.40	0.00	2.73	38.32	"
4506	U. S. P. Tahiti beans	0.11	0.00	21.75	20.00	0.00	1.75	38.84	"
4509	U. S. P. Tonka beans	0.00	0.21	....	....	...	...	....	"
4193	Commercial extract (not found adult'd)	0.08	0.00	21.84	10.36	8.87	2.61	40.00	"
4132	Commercial extract (not found adult'd)	0.18	0.00	13.52	0.90	10.76	1.86	27.51	"
4137	Commercial extract (not found adult'd)	0.15	0.00	16.43[2]	4 54	4.54	7.35[2]	21.27	"
4180	Commercial extract (not found adult'd)	0.09	0.00	16.72	15.44	0.00	1.28	20.90	"
4052	Commercial extract (not found adult'd)	0.22	0.00	22.66	20.00	0.00	2.66	23.79	"
4129	Adulterated commercial extract	0.22	0.08	0.86	0.47	0.00	0.39	6.34	artificial
4152	Adulterated commercial extract	0.68	0.15	14.00	10.64	2.42	0.94	17.32	natural
4179	Adulterated commercial extract	0.02	0.10	14.34[3]	0.75	0.00	13.59[3]	14.15	"
4141	Adulterated commercial extract	0.15	0.04	15.15	12.28	0.00	2.87	5.28	artificial
4078	Adulterated commercial extract	0.14	9.05	12.94	0.60	9.74	2.60	41.42	natural
4053	Adulterated commercial extract	0.24	0.18	14.62	10.92	0.00	3.70	11.91	"
4056	Adulterated commercial extract	0.07	0.00	14.35	11.20	0.00	3.15	31.72	artificial
3959	Adulterated commercial extract	0.06	0.23	36.16[2]	12.96	0.00	23.20[2]	7.53	"
3972	Adulterated commercial extract	0.01	0.09	13.44	11.14	0.00	2.30	9.68	"
3725	Adulterated commercial extract	0.44	0.11	26.54	21.00	0.00	5.54	10.73	"
4042	Adulterated commercial extract	0.06	0.05	35.50	31.88	0.00	3.62	13.36	natural

[1] Includes glycerin. [2] Contains glucose. [3] Contains invert sugar.

From the analyses of the U. S. P. samples it is evident that the percentage of vanillin bears no relation to the value of the extract. Sample No. 4562, made from Mexican beans costing $11.00 per pound, contained less than Nos. 4504 and 4505 made respectively from South American and Bourbon beans costing less than $7.00 per pound and but little more than No. 4506 made from Tahiti beans costing but $1.50 per pound. The average percentage of alcohol was 38.72 and of cane-sugar, 19.70. The residue other than cane-sugar ranged from 1.75 to 3.90 per cent. None of these extracts contained the slightest trace of coumarin; on the other hand, the Tonka bean extract contained 0.21 per cent. of coumarin but no vanillin.

The commercial extracts classed as "not found adulterated" appeared to have been made from vanilla beans, without addition of other coloring or flavoring matter. In most of these, however, the percentages of alcohol and sugar were less than in extracts prepared according to the Pharmacopoeia, and in some of them considerable amounts of glycerin (maximum 10.76 per cent.) or glucose were present, but these differences bear little or no relation to the value of the product.

All of the U. S. P. and the pure commercial extracts gave with lead acetate a bulky precipitate of a light brown-gray color and a filtrate from this precipitate of a light yellow color.

The adulterated samples contained vanillin in amounts ranging from 0.01 to 0.68 per cent. and nearly all of them contained coumarin in amounts up to 0.23 per cent. The minimum percentage of alcohol was 5.28 and of cane-sugar was 0.47. Glycerin was found in several samples, glucose in one and invert sugar in four. Many of these extracts gave only a slight precipitate with lead acetate, the precipitate as well as the filtrate being dark brown in color. After shaking the filtrate with fullers' earth and again filtering, colorless solutions were obtained in nearly all such cases, indicating that the color was due to caramel. In one extract only was a coal-tar color detected.

CONNECTICUT AGRICULTURAL EXPERIMENT STATION,
NEW HAVEN CONN., July 10, 1902.

[CONTRIBUTIONS FROM THE LABORATORY OF THE PENNSYLVANIA STATE COLLEGE AGRICULTURAL EXPERIMENT STATION.]

X. CREAMING OF MILK DURING ITS SALE.

BY WILLIAM FREAR AND M. H. PINGREE.

Received July 25, 1902.

THE theory that the creaming tendency of milk leads to a pronounced separation of this liquid into a fat-rich upper layer and fat-poor lower stratum under the conditions prevailing during the delivery of milk on a wagon-route or during its retailing in the shop, has sometimes been set up as a defense in prosecutions for adulteration of milk by skimming.

The experiments of Wing and Smith[1] satisfactorily show that milk delivered to customers on a wagon-route from a large can by means of a dipper that rests, when not in use, on the bottom of the can, is practically homogeneous. Dean[2] has shown that this is also true of milk that is distributed on a wagon-route, the liquid being delivered from large cans through a faucet.

The range of conditions that may occur during the retailing of milk from a shop, has not been so satisfactorily covered.

Carter Bell[3] examined a sample taken from two gallons of well-mixed milk to establish its initial composition. The milk was then set in a cool place and one pint withdrawn hourly, pains being taken to stir the milk as little as possible during the withdrawal; the total solids and fat in the fractions thus taken varied irregularly to the extent of 0.64 per cent.; there was no important separation of cream at any time; in fact, the last pint was richest in fat.

The writer has recently had occasion to consider the possibilities of separation under the following conditions: The sale of a small quantity of milk, kept in a jar set in a trough of cold water, delivered to customers in portions of a pint to a quart at irregular intervals during a period of six to eight hours, the milk being taken from the jar (without care to stir the contents) by means of a dipper, which is not returned to the jar but laid to one side during the intervals between sales to permit the close covering of the vessel.

In the experiment made to determine the effect of such con-

[1] Cornell Agricultural Experiment Station, Bulletin No. 20.

[2] Ontario Agricultural College, Bulletin No. 66.

[3] *Analyst*, No. 21, December, 1877; cited by Blyth: "Foods," 4th ed., p. 334.

ditions upon the final composition of the milk, a rather deep can was substituted for the jar, otherwise the conditions were exactly as stated above. Two gallons of milk were used, having first been thoroughly mixed and sampled at 8.30 A.M.; at times stated, below, quantities of approximately one pint were withdrawn by a scooping motion of the dipper. The fractions thus withdrawn were analyzed by the usual creamery methods, *i. e.*, the fat was determined by the Babcock test, in duplicate; the duplicates gave identical results in all but two instances, where differences of 0.10 per cent. occurred. The density was determined by use of a Quevenne lactometer, with due correction for temperature variations; the readings were made to one-fifth degree, though the tendency of milk to coat the stem and obscure the scale of the lactometer makes it doubtful whether an accuracy of more than one-half to one-third degree is possible. The total solids were computed from the data thus obtained, by use of the Babcock short formula:

$$\text{Total solids} = \frac{L}{4} + 1.2f,$$

where L represents the Quevenne lactometer reading corrected to 60° F., and f represents the percentage of fat in the milk. Owing to the limitations of the lactometric method mentioned above, it is doubtful whether the solids determinations can be made more closely than 0.08 to 0.12 per cent.

The entire detail of the experiment was carried out by M. H. Pingree.

The results obtained were as follows:

Time.	Fat. Per cent.	Quevenne lactometer readings, (60° F).	Total solids. Per cent.	Solids, not fat. Per cent.
8.30 A.M.	4.35	34.0	13.72	9.37
10 A.M.	7.45	31.1	16.69	9.24
11 A.M.	7.20	32.0	16.64	9.44
12 M.	6.10	32.8	15.52	9.42
2 P.M.	5.90	32.8	15.28	9.38
2.30 P.M.	4.80	33.4	14.11	9.31
4 P.M.	4.10	34.3	13.49	9.39

It is probable that the lactometer reading at 10 A.M. was slightly too low; otherwise the analytical results check within the allowable limits of error.

The results show very clearly that customers buying the second to sixth portions of milk inclusive, would receive much more than their share of the fat, and the last comers a greatly impoverished milk, when the conditions of sale resemble those of this experiment.

NEW BOOKS.

ON CANE-SUGAR AND THE PROCESS OF ITS MANUFACTURE IN JAVA. By H. C. PRINSEN GEERLIGS. Published in the office of the *Sugar-Cane*, Altrincham.

This book contains brief statements of the chemical compositions of the sugar-cane. In addition to the cane-sugar, which is the principal constituent from a technical standpoint, the sugar-cane consists of water and cellulose or fiber. The fiber is about 70 per cent. pure cellulose and 30 per cent. wood-gum or xylan. The organic acids are glycolic, malic, succinic and small quantities of tannic. Citric, tartaric, and aconitic acids are said by some investigators to exist in normal sugar-cane, but these statements lack confirmation. The lime salts of these organic acids are soluble and are therefore not removed by clarification. From a technical point of view the organic acids which are formed by the action of lime during evaporation of the juices are of quite as much importance as those which exist naturally in the cane. These latter acids are lactic, saccharinic, gluconic, and saccharic. Acetic acid only exists in cane which has undergone fermentation.

The nitrogenous bodies of the cane are chiefly albumen, amides, or amino acids and xanthine bases. It is not certain whether the amides or amino acids consist of asparagine, aspartic acid or glycocol, Xanthine bases are composed chiefly of guanine. The total nitrogen in a mature sugar-cane does not exceed one-tenth of 1 per cent.

The coloring-matters of the cane are chiefly chlorophyll and its alteration products and anthocyan. There is also another coloring-matter in the fiber which becomes yellow on contact with alkaline liquids. The cane wax which exists on the outside of the cane is soluble in alcohol, ether, chloroform and benzine. It is not a wax properly so-called, but a saturated alcohol, having 24 atoms of carbon. In addition to the sucrose, levulose, and dextrose which form the chief part of the soluble carbohydrates, the

cane also contains a small quantity of pectin. The ash of the cane is composed chiefly of potash and silica. Small quantities of soda, lime, magnesia, oxide of iron and sulphuric acid are also found in the ash.

The technical part of the work gives in a condensed form a statement of processes of manufacture which obtain on the island of Java. The articles on clarification, filtration and evaporation will be found useful to those engaged in technical sugar work.

Every one who is engaged in the manufacture of sugar will find Mr. Geerligs's book practical and full of useful suggestions.

H. W. WILEY.

THE GAS ENGINEER'S LABORATORY HANDBOOK. By JOHN HORNBY. Second edition, revised and enlarged. London, E. & F. N. Spon. New York: Spon and Chamberlain. 1902. xvi + 304 pp.

This volume describes the various analytical operations that are necessary to the proper control of the manufacture of illuminating gas. Parts I, II, and III (112 pages) are devoted to the consideration of elementary quantitative analysis, the topics there discussed being the balance, weights and weighing, sampling, precipitation, filtration, gravimetric determinations and volumetric analysis. Part IV deals with the special analyses required in gas works, such as the analyses of coal and coke, the examination of crude gas, testing of purified gas, analysis of ammoniacal liquor, lime, limestone, oxide of iron, spent oxide and fire-clay, the assay of coal-tar, fractional distillation and the determination of the specific gravity of gases. In Part V, technical gas analysis, calorimetry and the examination of oils are considered. The Appendix contains the English Gas Referees' Instructions concerning the examination of the purity of illuminating gas, and these are followed by various useful tables.

The book contains only what is essentially English practice, and recent improvements in methods and procedures that have been adopted in Germany and in this country have rarely been incorporated by the author. For example, the method for the analysis of coal as recommended in the Report, to the American Chemical Society, of the Committee on Coal Analysis is not even referred to, and the many recent improvements in the methods of analysis of gas mixtures appear to have escaped the author's attention. The work contains, however, much valuable and interesting informa-

tion and will be found a convenient book of reference by those who have to do with the manufacture and analysis of illuminating gas.

L. M. DENNIS.

GUIDE TO PREPARATION WORK IN INORGANIC CHEMISTRY. BY DR. BLOCHMANN; translated by JAS. LEWIS HOWE. Published by Washington and Lee University, Lexington, Virginia. Price, 60 cents.

The translation of Blochmann's "Anleitung zur Darstellung chemischer Präparate" by Professor James Lewis Howe places this excellent little book within reach of students who are unable to read it in the original. While the demand for an elementary text in inorganic preparations is perhaps not so great as it is abroad, inasmuch as many of our texts in general chemistry include considerable work of this nature, nevertheless, too much emphasis can not be placed upon the making of inorganic compounds in exactly the line followed by Blochmann; namely, determining the amount of pure substance which can be made from a given amount of raw material.

Most of the processes given are simple but important, and if faithfully followed out, will give the student a pretty clear idea of the common methods used in making of these simpler inorganic substances. In fact, it would seem that the book might be used to advantage by advanced students of general chemistry before they have had the work in analytical chemistry mentioned by the author.

Several of the first experiments are found in nearly all of our texts on general chemistry, the only difference being that the quantitative results emphasized here, are usually omitted in general chemistry. Among these preparations are hydrochloric acid, nitric acid, ammonia, sodium hydroxide, sodium nitrite, iron sulphate, disodium phosphate and the acids of phosphorus. Among the less common ones are urea, hydroxylamine, crystallized silicon, antimony trichloride and amidosulphonic acid.

While the text is scarcely large enough for a full course in inorganic preparations, it might be used in connection with a course in advanced chemistry with good results. Indeed it is to be hoped that the time will soon come when much of the advanced work in general chemistry will be along the line indicated in this little book.

G. B. FRANKFORTER.